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CONTENTS

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LATERAL SUPPORT OF STEEL COLUMNS AND STRUTS[1]

BY C. R. YOUNG[2] AND W. B. DUNBAR[3]

Abstract

Experimental investigation of 19 full-size steel columns was undertaken to disclose *(a)* the merit of a lateral stay member that does not fix the direction of the column at the point of support, *(b)* the effectiveness of a stay member that connects to one edge only of the column width, *(c)* the effect on the required lateral support of initial column curvature or eccentricity, and *(d)* the maximum stress for which a stay member should be proportioned.

The results obtained appear to warrant the following conclusions:

(1) The percentage increase in the ultimate capacity of columns due to the introduction of lateral support is greatest for columns with high slenderness ratios and least for those with low slenderness ratios.

(2) For a column hinged at both ends, and having end eccentricity of loading up to one-eighth of the column width in the direction of bending, the introduction of lateral support at mid-height, without rotational fixing at this point, raises the strength to from 2.70 to 4.87 times the theoretical strength of the full-length column as computed by the secant formula.

(3) The necessary lateral supporting force of an eccentrically loaded, deflected column, where the lateral force is applied at the middle of the width of the section, is given with sufficient exactness by Equation (22),

$$Q_w = \frac{5P}{l}(\Delta \pm 1.33e) - \frac{48EIn}{l^3}.$$

(4) The relation between the necessary lateral supporting force applied at the edge of the section and that applied at the middle of the section width for a given deflection of the flange under consideration is given satisfactorily by Equation (23). For the test columns, which had widths of section normal to the plane of bending varying from 6 in. to 15⅜ in. and were subjected to loads up to 2.5 times the Euler load for a laterally unsupported column, the lateral supporting force when applied to the edge of a flange was in no case more than 15% greater than that which would have been necessary if applied to the middle of the web at the same flange deflection.

I. Introduction

1. Nature of the Problem

The capacity of a column or strut of a given cross section and length is admittedly greatly increased by preventing it from deflecting laterally at, or near, the point where this deflection would be greatest if no support were provided. The amount of the benefit has, however, been a matter of some uncertainty, as has the necessary capacity of the supporting or stay member serving to shorten the column.

Some of the questions that have been raised are:

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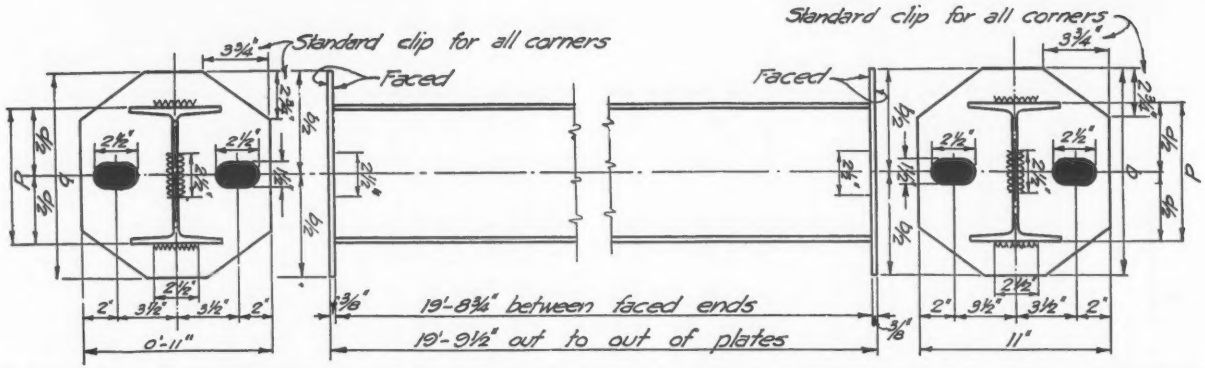


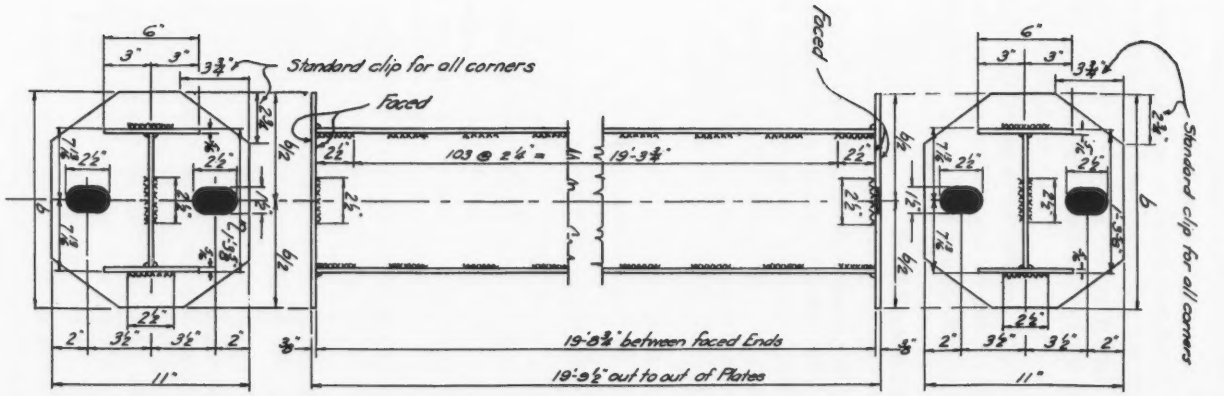
No. of specimens	Mark	Section	Plate	
			Stock	*b*
3	*C1A, C1B, C1C.* (alike)	6 in. – 17.25 # I	11 × ⅜ in.	9 in.
2	*C2A, C2B.* (alike)	7 in. – 20.0 # I	11 × ⅜ in.	10 in.
2	*C3A, C3B.* (alike)	10 in. – 16.5 # B.J.	11 × ½ in.	1 ft. – 1 in.
2	*C4A, C4B.* (alike)	9 in. – 25.0 # I	11 × ½ in.	1 ft. – 0 in.
2	*C5A, C5B.* (alike)	12 in. – 31.8 # I	11 × ½ in.	1 ft. – 3 in.
2	*C6A, C6B.* (alike)	9 in. – 20.5 # CM.	11 × ½ in.	1 ft. – 0 in.
2	*C7A, C7B.* (alike)	10 in. – 28.5 # B	11 × ½ in.	1 ft. – 1 in.
2	*C8A, C8B.* (alike)	12 in. – 28.0 # C	11 × ½ in.	1 ft. – 3 in.

Fillet welds ⅜ by ⅜ in.

NOTE

1. Column shaft must be perfectly straight.
2. Ends of columns to be faced absolutely parallel, not merely ground or chipped, before welding on plates.
3. Plates to be located centrically and have full contact over faced ends of column when welded.
4. Outside faces of plates to be faced absolutely parallel, not merely ground or chipped, after welding to faced column ends.
5. Plates may be ½ in. or 7/16 in. thick, but must not be more than ¾ in. thick after final facing.
6. Final length of column out to out of plates must be exact.
7. Initial length of column shaft to be about 6 in. longer than finally required. This 6 in. length to be cold sawn from shaft, marked same as column, and delivered to purchaser.

FIG. 1. *Schedule of rolled columns.*



Column			End plates			Mark
No. required	Plates	Length	Stock	*b*	Slot	
2	2 — 6 in. × 5/16 in., 1 — 15 in. × 5/16 in.	19 ft. – 8¾ in.	11 × ½ in.	1 ft. – 6 in.	2½ × 1½	*C9A* and *C9B*

NOTE

1. Column shaft must be perfectly straight after welding.
2. Ends of column to be faced *absolutely parallel*, not *merely* ground or chipped *before welding* on plates.
3. Plates to be located centrically and have full contact over faced ends of column, when welded.
4. Outside faces of end plates to be faced *absolutely parallel, not merely* ground or chipped, after welding to faced column ends.
5. Plates may be ½ in. or 7/16 in. thick but must not be more than ½ in. thick after final facing.
6. Final length of column out to out of plates must be exact.
7. *Welding of flange plates to the web to be carried on in a way to prevent local warping between welds or general warping of whole column.*
8. ¼ in. fillet welds.

FIG. 2. *Schedule of welded columns.*

(a) What is the merit of a stay member that does not fix the direction of the column at the point of support?

(b) How effective is a stay member that connects to one edge only of the column width, as, for example, a girt to a side column of a mill building?

(c) How is the value of a given lateral support affected by initial column curvature, or by eccentricity, either in the direction of the initial curvature, or in the opposite direction?

(d) For what axial load should a stay member be designed for the most critical of the above conditions?

The investigation here reported was directed to the answer of these and related questions.

II. Experimental Work

2. *Specimens*

All the test columns were made free to turn at the ends and were 20 ft. long between centres of end pivots. The testing equipment available restricted to 310,000 lb. the maximum axial load that could be applied. Within these limits the sections were so chosen, as is evident from Table I, as to give a progression in the maximum slenderness ratio of roughly 30, taking the length, l, for this purpose as the full length of the column, centre to centre of pivots.

TABLE I

PROPERTIES AND ULTIMATE LOADS OF THE TEST COLUMNS

All columns were 20 ft. long, centre to centre of pivots

Column mark	Section	Area, A, sq. in.	Minimum radius of gyration r, in.	Maximum slenderness ratio $\frac{l}{r}$ for l = 240 in.
C1A	6-in., 17.25-lb. I	5.02	0.68	353
C1B	6-in., 17.25-lb. I	5.02	0.68	353
C1C	6-in., 17.25-lb. I	5.02	0.68	353
C2A	7-in., 20-lb. I	5.83	0.74	324.3
C2B	7-in., 20-lb. I	5.83	0.74	324.3
C3A	10-in., 16.5-lb. B.J.	4.86	0.79	303.9
C3B	10-in., 16.5-lb. B.J.	4.86	0.79	303.9
C4A	9-in., 25-lb. I	7.28	0.88	272.9
C4B	9-in., 25-lb. I	7.28	0.88	272.9
C5A	12-in., 31.8-lb. I	9.26	1.01	237.7
C5B	12-in., 31.8-lb. I	9.26	1.01	237.7
C6A	9-in., 20.5-lb. C.M.	6.02	1.15	208.7
C6B	9-in., 20.5-lb. C.M.	6.02	1.15	208.7
C7A	10-in., 28.5-lb. B.	8.41	1.30	184.6
C7B	10-in., 28.5-lb. B.	8.41	1.30	184.6
C8A	12-in., 28-lb. C.	8.22	1.53	156.9
C8B	12-in., 28-lb. C.	8.22	1.53	156.9
C9A	1—15 × 5/16-in. pl. 2— 6 × 5/16-in. pls.	8.44	1.16	206.9
C9B	1—15 × 5/16-in. pl. 2— 6 × 5/16-in. pls.	8.44	1.16	206.9

Nineteen columns were fabricated and tested. Seventeen of these were simple rolled sections, ranging from a 6-in., 17.25-lb. I to a 12-in., 28-lb. C, as shown in Fig. 1. Two were sections built up of three plates into I-form by welding, as shown in Fig. 2. The depth of these sections, 15⅝ in., was made as great as could be accommodated in the machine, after making provision for the necessary auxiliary loading equipment.

3. Testing Equipment

As the available 400,000 lb. Riehlé testing machine could not, with the type of roller end bearings adopted for the test columns, accommodate columns more than 9.4 ft. long between end pivots, it was necessary, in order to load a specimen, to offset it 2 ft. 2 in. from the centre of the machine and to allow it to pass through the floor above. A test specimen, partly obscured by the near standard of the machine, is seen in position for test in Fig. 3.

The load was applied to the top of the column by means of two built-up loading eye-bars bolted to a loading cap. The necessary pull in these eye-bars was developed by pin-connecting them at the lower end to an end panel point of a loading truss, to the apex joint of which the testing machine applied through a spherical head any load up to the capacity of the machine. The far support of this truss is shown at the right in Fig. 3.

Lateral loads were applied to the test column by means of one or other of two gauge-equipped, 12-ton, horizontally placed hydraulic jacks. Each of these bore against a vertical lateral-loading beam, shown to the left in Fig. 3. Test columns were so oriented that the buckling would always take place in a plane parallel to the plane of the web of the lateral-loading beam, that is, either to the North (to the right in Fig. 3) or to the South.

In order that the buckling of the column in either sense might be met by a compressive, rather than a tensile, force, the test column, eye-bars, and lateral loading beam were girdled by a lateral loading frame carried on ball bearings moving on another support frame suspended as shown in the upper left-hand corner of Fig. 3 and in Fig. 4. If the test column tended to buckle to the North, its movement could be resisted by one jack forcing the frame with the attached loading screw, which bears against the column, to the South. If the column tended to buckle to the South, its movement could be countered directly by the other jack.

To reduce the uncertainty that frequently arises with respect to the degree of restraint existing at the ends of a column, and to be able to relate the actual to the theoretical performance, the test column was loaded at each end through roller bearings, especially manufactured for this research. These showed an average coefficient of friction under actual operating conditions of only about 0.0002.

The hydraulic jacks were provided with gauges originally intended for reading the lateral loads. It was found, however, that the friction on the ram was such a large factor in the comparatively small lateral loads that

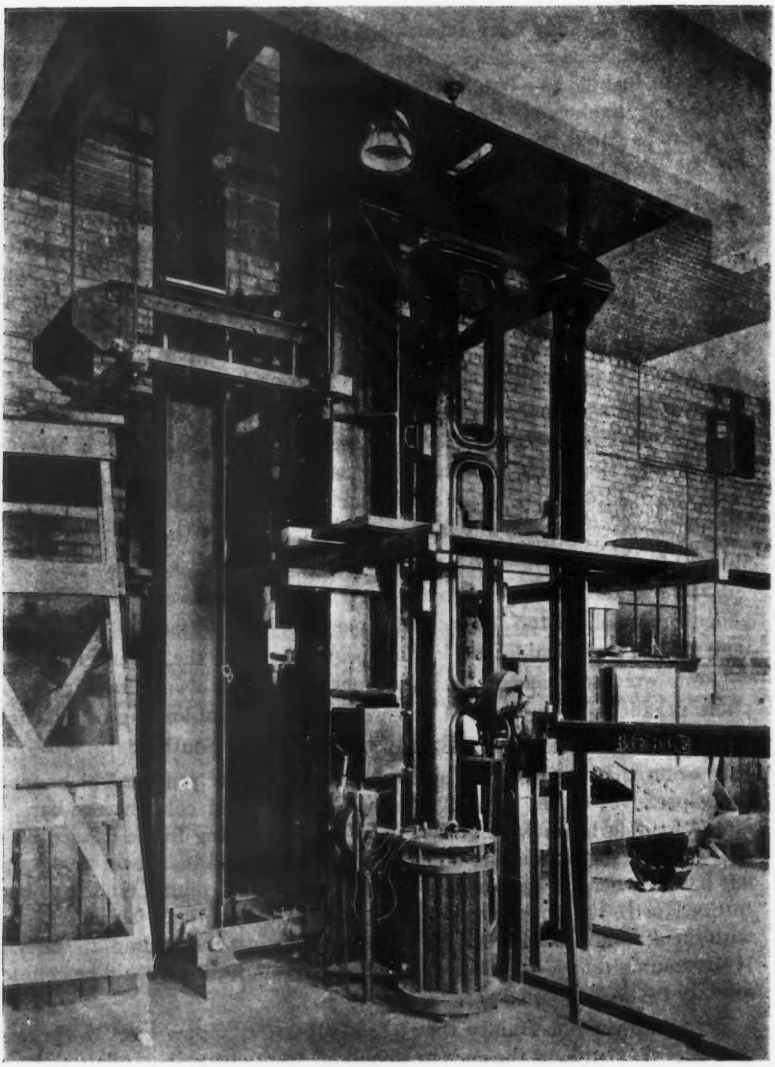


FIG. 3. *General view of testing apparatus from the Southeast.*

reliance could not be placed on the gauges. Friction also prevented the flexibility that was desirable in applying the loads.

For this reason, spring dynamometers of 1000 lb., and later 3000 lb., capacity (3) were developed. These were used on the head of the jacks and were read in place of the gauges on the jacks.

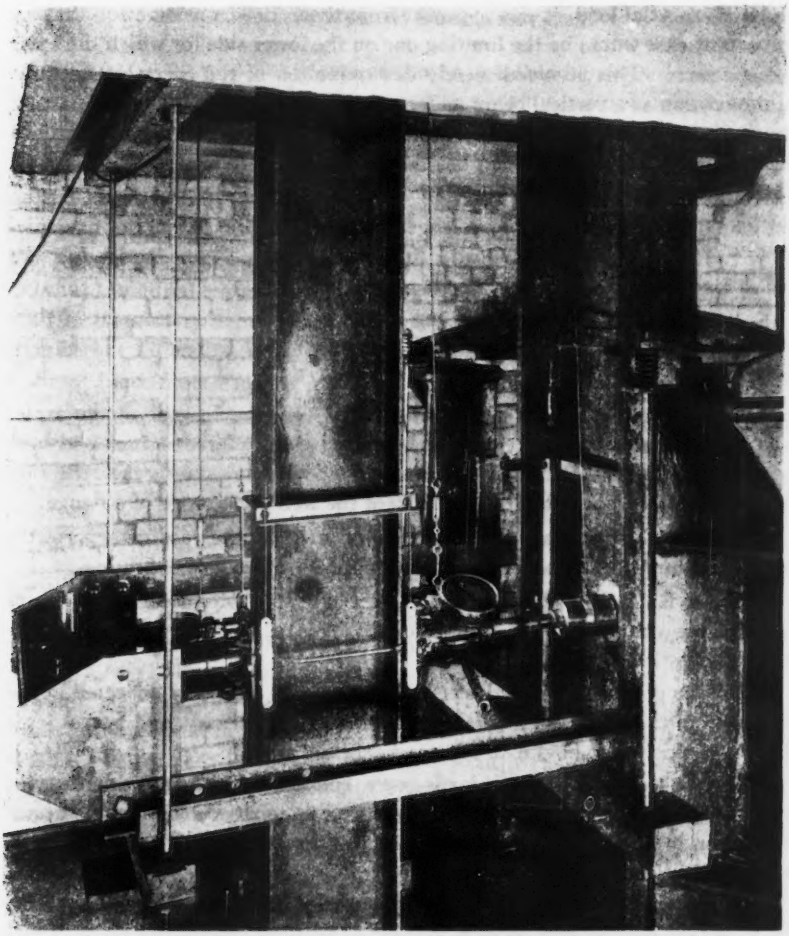


FIG. 4. *Jacks and dynamometer in position for web support, portion of lateral loading frame being removed.*

In order that the test column might not be subjected to a large initial dead load, a counterbalancing steelyard device was introduced between an overload trolley and the lifting eye in the loading cap, whereby the column was relieved of the dead load tension in the loading eye-bars, the weight of the loading cap and the upper roller bearing. The only initial load on the column was, therefore, its own weight.

4. Testing Procedure

General. One of the objectives of the investigation being the determination of the necessary lateral supporting force at mid-height with a given deflection

and a given axial load, it was apparent from theoretical consideration that an important case would be the limiting one on the lower side for which the axial force is zero. This involved merely determination of the central deflections of the column as a vertical beam under a single central load. The line passing through the points representing the relation of lateral deflection to lateral load when no axial load existed has been called the zero load line.

It was found convenient, in general, to relate the applied loads to the estimated Euler load, based on a length of 240 in., making them, for example, $\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$, 1, and $1\frac{1}{2}$ times that load. In all cases, at least one load below the Euler load, in addition to the zero load, was used.

For the purpose of computing the Euler load from Equation (1) of Part III, actual values of EI were determined from observations on the column acting as a vertical beam.

Although the deflections of the two flanges were not in general the same, all diagrams indicating the relation of lateral supporting force to axial load were so plotted that the deflection indicated on the horizontal scale is the deflection of the supported point, be it the middle of the web or the edge of a flange.

Centric load. For loads below the Euler load, in the case of a perfectly straight column, a lateral load had to be applied to produce deflection.

For the Euler load, the various deflections were produced without any appreciable change in the lateral force. This is in accordance with the theory of action of the Euler column.

For loads greater than the Euler load the column naturally deflected in the direction of the initial curvature or unavoidable eccentricity, and lateral force had to be applied to hold it to a desired deflection.

Eccentric loads. Eccentric loads were handled in the same manner as centric ones, with the exception that there was no tendency to take up natural deflection in a direction opposed to the eccentricity within the desired maximum deflection.

The plotted results for the earlier columns indicated that they were acting in a certain regular and definite manner. All lines representing axial loads intersected at a point on the zero load line. For eccentric loads this intersection point moved outward from the origin to the North or South, according as the eccentricity of loading was North or South. The amount of this movement was found to be approximately $\frac{4}{3}e$, where e is the eccentricity of application of the load. The lateral supporting force was, therefore, the same for all axial loads when the deflection was equal to this amount. From observation it appeared that the cylindrical end bearings were at their greatest distance apart at this deflection, since the loading head of the machine had to be lowered for deflections on either side of this point. Theoretical calculations later substantiated this belief.

III. Theoretical Considerations

5. General

Given a column with imperfections that may be readily represented mathematically, it is possible to develop expressions for the central transverse supporting load consistent with the axial load, the properties and peculiarities of the column, the eccentricity, and the deflection.

In the general case, allowance must be made for initial crookedness in the column. It is not practicable to take account mathematically of local kinks, but it is entirely feasible to include the effect of smooth initial curvature. Investigations have been made on the basis of three assumptions, namely, *(a)* that the initial curve is a sinusoid, or the deflection curve of a centrically loaded long column, *(b)* that it is parabolic, and *(c)* that it is the same as that for a simply supported beam subjected to a central transverse load.

6. Euler Load, Ends Pivoted

For centrically loaded, perfectly straight, homogeneous columns of such slenderness ratio that failure may occur by buckling before the elastic limit of the material is reached, the ultimate, or Euler, load is given by the formula

$$P_e = A \cdot \frac{\pi^2 E}{\left(\frac{l}{r}\right)^2} = \frac{\pi^2 EI}{l^2}, \tag{1}$$

in which A = area of the column;
E = modulus of elasticity of the material;
l = length of the column applicable to the direction of buckling;
r = radius of gyration in the direction of the buckling.

Within this load the column will remain perfectly straight; there will be no lateral deflection, no bending moment and, in theory, no need for lateral support. If the Euler load be exceeded ever so little the column will suddenly buckle sideways and collapse owing to form change, or springiness. The exact Euler load will hold the column at any deflection put in it by a lateral force temporarily applied and removed.

7. Lateral Supporting Force for Eccentric Loading

The lateral supporting force will be found by taking into account the actual curve produced in the column by the forces acting on it, evaluating in the one process the net effect of the force that the column by reason of its geometrical form tends to exert against a theoretical stop placed at mid-height and the spring-back effect. In certain instances a negative sign will be found associated with the lateral supporting force. This indicates that it is necessary to force the column out into the deflected position indicated by the application of a force Q in the sense of the bulge.

Since the natural crookedness of a column is irregular and unpredictable, the assumption that the initial curve is a sinusoid is as good as any other. If the deviation at the centre is c, then

$$z = c \sin \frac{\pi x}{l} \tag{2}$$

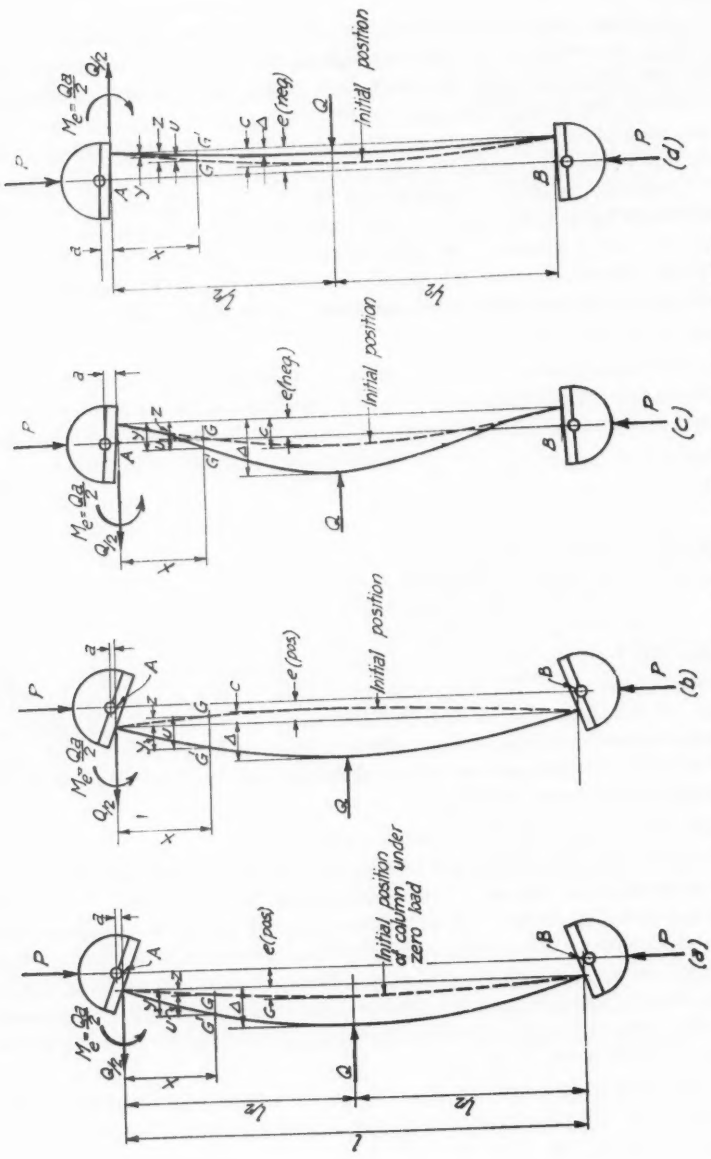


FIG. 5. *Lateral supporting force, Q, for columns subjected to eccentric axial loading.*

Case (a). Consider the column shown in Fig. 5*(a)*. Any general point G on the unstressed column will move, under the system of applied forces, to G', or through a horizontal distance u. The distance y of the point G' from the straight line joining the ends of the column is thus made up in part of an initial no-stress deviation z and an elastic deviation or deflection u; that is,

$$y = u + z \tag{3}$$

The moment at the point G', if we count clockwise moments on the portion of the column above G' as positive, is

$$M = P(u + z + e) - \frac{Qx}{2} - \frac{Qa}{2} \tag{4}$$

Let the origin be at A, the point where a horizontal line through the end of the column shaft cuts the load line. Let x be positive when measured downward, and e, z, u, and y be positive if measured to the left. Then,

$$\frac{d^2u}{dx^2} = -\frac{M}{EI}.$$

Proceeding along the general lines of J. E. Boyd's analysis (1) and inserting the value of M from Equation (4), and z from Equation (2),

$$\frac{d^2u}{dx^2} + \frac{Pu}{EI} = -\frac{Pc}{EI}\sin\frac{\pi x}{l} - \frac{Pe}{EI} + \frac{Qx}{2EI} + \frac{Qa}{2EI} \tag{5}$$

Solving this equation, evaluating the constants, introducing the value of z given in Equation (2), and noting that when $x = \frac{l}{2}$, $y = \Delta$,

$$\Delta = \frac{\frac{c\pi^2}{l^2}}{\frac{\pi^2}{l^2} - \frac{P}{EI}} + \left(e - \frac{Qa}{2P}\right)\sec\sqrt{\frac{P}{EI}}\cdot\frac{l}{2}$$

$$- \frac{Q}{2P}\sqrt{\frac{EI}{P}}\tan\sqrt{\frac{P}{EI}}\cdot\frac{l}{2} - e + \frac{Ql}{4P} + \frac{Qa}{2P}. \tag{6}$$

Now, if for further simplicity we let $m = \sqrt{\frac{P}{EI}}$

$$\sqrt{\frac{P}{EI}}\cdot\frac{l}{2} = \alpha, \text{ and } \frac{\frac{c\pi^2}{l^2}}{\frac{\pi^2}{l^2} - \frac{P}{EI}} = rc,$$

and replace (sec α − 1) by exsec α, we may write finally for Case (*a*)

$$Q = \frac{2P\,(rc + e\,.\,\text{exsec}\,\alpha - \Delta)}{a\,.\,\text{exsec}\,\alpha + \frac{1}{m}\tan\alpha - \frac{l}{2}}. \tag{7}$$

Case (b). As is evident from Fig. 5*(b)* the only difference between Case *(a)* and Case *(b)* is that the initial crook is opposite in sense to the deflection Δ. Equation (7) is, therefore, applicable if a negative sign is attached to the first term in the numerator and the arithmetic value of c is employed. We then have

$$Q = \frac{2P(-rc + e \cdot \text{exsec } \alpha - \Delta)}{a \cdot \text{exsec } \alpha + \frac{1}{m} \tan \alpha - \frac{l}{2}}. \tag{8}$$

Case (c). Except for negative eccentricity, Case *(c)* is the same as Case *(a)*. Introducing the negative sign for the second term in the numerator of Equation (7), and using the arithmeric value of e, there results

$$Q = \frac{2P(rc - e \cdot \text{exsec } \alpha - \Delta)}{a \cdot \text{exsec } \alpha + \frac{1}{m} \tan \alpha - \frac{l}{2}} \tag{9}$$

Case (d). Case *(d)* is analogous to Case *(c)* in that the sense of c, e, and Δ is relatively the same. Equation (9) consequently applies. The sense of the lateral supporting force will depend on the relative values of the three terms in the numerator.

8. Force Required to Produce a Given Deflection of a Flange when Applied in Its Plane, and with Zero Axial Load

Preliminary to a consideration of the lateral supporting force required for an axially loaded column when the force is applied at the edge of a flange, and parallel thereto, rather than at the middle of the web, it is desirable to ascertain the relation between a force applied to a flange and the resulting deflection of that flange, P being zero.

The total deflection of the loaded flange of a straight column, as indicated in Fig. 6*(a)*, is

$$\Delta = \Delta_1 + \Delta_2, \tag{10}$$

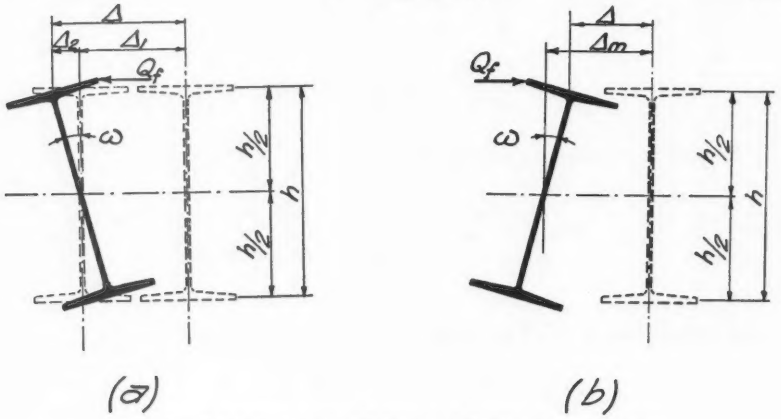


FIG. 6. *Relation of mean deflection to deflection of loaded flange.*

where Δ_1 = deflection if the lateral force Q were applied at the middle of the web of the column, and,

Δ_2 = additional deflection due to the torque, which arises from the application of Q_f at a flange centroid, that is, at $h/2$ from the centre of the cross section.

For a transverse force Q_f applied at mid-height of a column of length l, with perfectly hinged ends, the centre deflection is

$$\Delta_1 = \frac{Q_f l^3}{48EI} . \tag{11}$$

As is evident from Fig. 6 *(a)*, the added deflection at the loaded flange due to the torque is

$$\Delta_2 = \omega \cdot \frac{h}{2} ,$$

the angle ω being the total twist angle developed in the half length, $l/2$, of the column.

Now, under the constant torque, T, existing in the half length, this twist angle is

$$\omega = \frac{Tl}{2E_s J} , \tag{12}$$

where E_s = shearing modulus of elasticity, and,

J = torsional stiffness factor, which may be determined by experiment or, approximately, by empirical formula.

Values of J for the various sections tested were computed by the method of Lyse and Johnston (2).

For a torque applied at mid-length of a column, the torque in either half length is

$$T = \frac{Q_f}{2} \cdot \frac{h}{2} = \frac{Q_f h}{4} ,$$

where h is the distance between flange centroids. The twist angle at mid-length becomes, therefore,

$$\omega = \frac{Q_f hl}{8E_s J} , \tag{13}$$

and it follows that

$$\Delta_2 = \frac{Q_f h^2 l}{16E_s J} . \tag{14}$$

Substituting in Equation (10) the values of Δ_1 and Δ_2 obtained from Equations (11) and (14) and solving,

$$Q_f = \frac{48EI\Delta}{l^3 + \dfrac{3EIh^2 l}{E_s J}} . \tag{15}$$

The effect of the torsion is obviously represented by the second term in the denominator.

9. Lateral Supporting Force Required for Axially Loaded Column when Applied at Flange Centroid

When a lateral supporting force holds a flange at a deflection Δ, while the mean deflection of the cross section is Δ_m, Fig. 6*(b)*, the amount of work that has had to be done by it is the same as the amount that would have to be done by a force applied at the middle of the web and holding the whole cross section to a deflection of Δ_m. This is true because the moment and deflection effects produced by the advanced position of one-half of the section beyond Δ_m are offset by the effects of the equally retarded position of the other half.

Experiment confirms this. Studies of the relative lateral supporting forces for flange-supported and web-supported columns show that with flange support the lateral supporting force for a given mean deflection equals the lateral supporting force for a web-supported column with a deflection equal to the mean for the flange-supported one.

If, then, the mean deflection could be found or predicted, it would be possible to utilize, for flange support, formulae and diagrams for web-supported columns, employing mean deflections in all cases.

As Δ_m is not known beforehand, it is desirable to express it in terms of a known deflection, that is, Δ.

Now, the mean deflection for the case of positive lateral supporting force, Q_f, Fig. 6*(b)*, is

$$\Delta_m = \Delta + \frac{Q_f h^2 l}{16 E_s J}. \tag{16}$$

If it should happen that the axial load is such that lateral force has to be exerted to cause the column to move out to the desired deflection, Q_f becomes negative and the mean deflection is less than Δ.

Since the lateral supporting force for a flange-supported column equals the lateral supporting force for a web-supported column with a deflection Δ_m, the latter may be inserted as the value of Δ in Equation (7). Then

$$Q_f = \frac{2P(rc + e \,.\, \text{exsec}\ \alpha - \Delta_m)}{a \,.\, \text{exsec}\ \alpha + \frac{1}{m} \tan \alpha - \frac{l}{2}}.$$

Inserting the value of Δ_m from Equation (16), and letting the denominator be represented by D, we have

$$Q_f = \frac{2P(rc + e \,.\, \text{exsec}\ \alpha - \Delta)}{D} - \frac{PQ_f h^2 l}{8DE_s J}.$$

The first term of the right-hand member of this equation is obviously equal to the support necessary for a web-supported column with deflection equal to Δ, the deflection imposed upon the supported flange of the flange-supported column. Letting this term be Q_w, there follows

$$Q_f = \frac{Q_w}{1 + \frac{Ph^2 l}{8DE_s J}}. \tag{17}$$

Equation (17) relates the desired flange force to the web force necessary to maintain a mean deflection in the section equal to any arbitrarily selected deflection for the supported flange.

IV. Analysis of Results

10. General

The principal test results were set out for consideration in 20 diagrams, of which Fig. 7, relating to column 9*A*, is typical. These showed the relation between applied lateral force, deflection, and axial load on the column for both centric and eccentric loads and for lateral support applied either to the middle of the web or to the edge of a flange. The deflection indicated on the horizontal scale is the deflection of the supported point, as indicated in Fig. 6. Fig. 8 gives the characteristic relation of the lateral force to varying axial load for columns *C1A* to *C4B*. Figs. 9, 10, 11, and 12 indicate the nature of the column curvature for the columns when the deflection of either the web or a flange at mid-height of the column is held at zero.

11. Comparison of Theoretical with Experimental Results

It was thought desirable to indicate on the lateral-force–deflection diagrams, such as Fig. 7, certain points that would lie on the theoretical lines of lateral-force–deflection, but, to avoid confusion, these lines have not been drawn in. The points are indicated for an approximate theory, as represented by the equations

$$Q = \frac{4.87P(\Delta + 1.23e)}{l} - \frac{48EIn}{l^3} \tag{18}$$

and

$$Q_f = \frac{Q_w}{1 + \dfrac{h^2 l}{16E_s J}\left\{\dfrac{48EI}{l^3} - \dfrac{4.87P}{l}\right\}}, \tag{19}$$

where n = the central deflection of the column from its unstrained position, and for the so-called exact theory, as represented by Equations (7) and (17). The first right-hand term of Equation (18) represents the approximate value of the force that the column by reason of its geometrical properties only would bring to bear against an imaginary stop placed against it at mid-height, and the second term, the spring-back effect due to the elastic properties of the column. Points have also been indicated on the lines that would be drawn in the construction of the Jackson diagram, the nature of which is described in Art. 12.

In plotting the points for these theoretical lines it was necessary to place the origin in such a position as to take account of any accidental or unpredictable eccentricity effects that may have been revealed by the tests but for which no allowance is made in the formulae.

12. Jackson Diagram

An interesting method of determinating the necessary lateral supporting force for a column subjected to centric or eccentric loading is available through the construction of a diagram proposed by Prof. K. B. Jackson and later

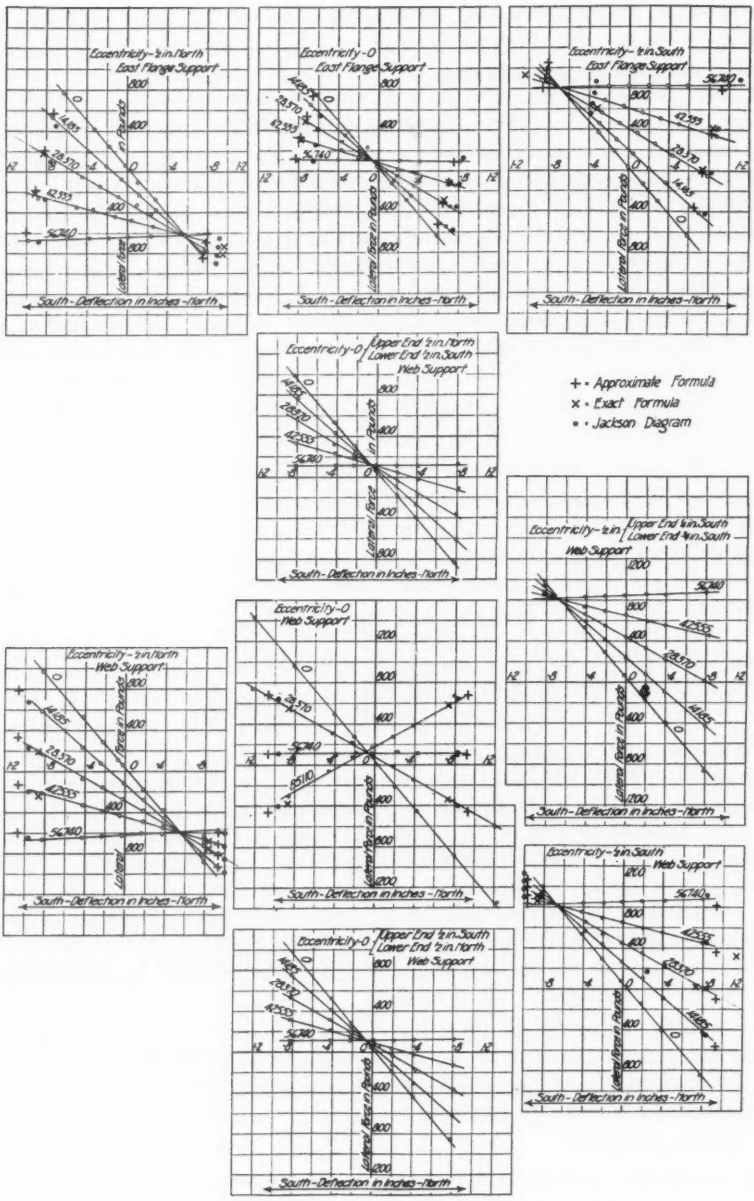


FIG. 7. *Lateral-force–deflection diagrams for Column C9A.*

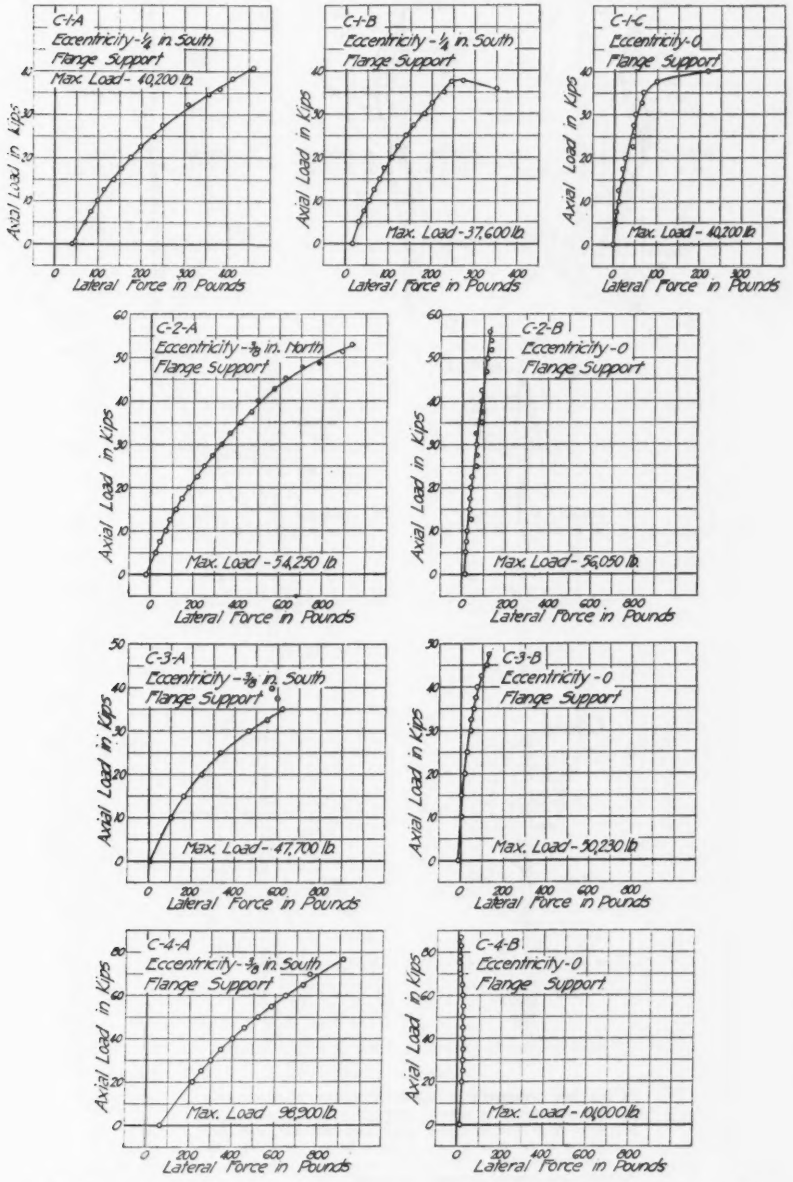
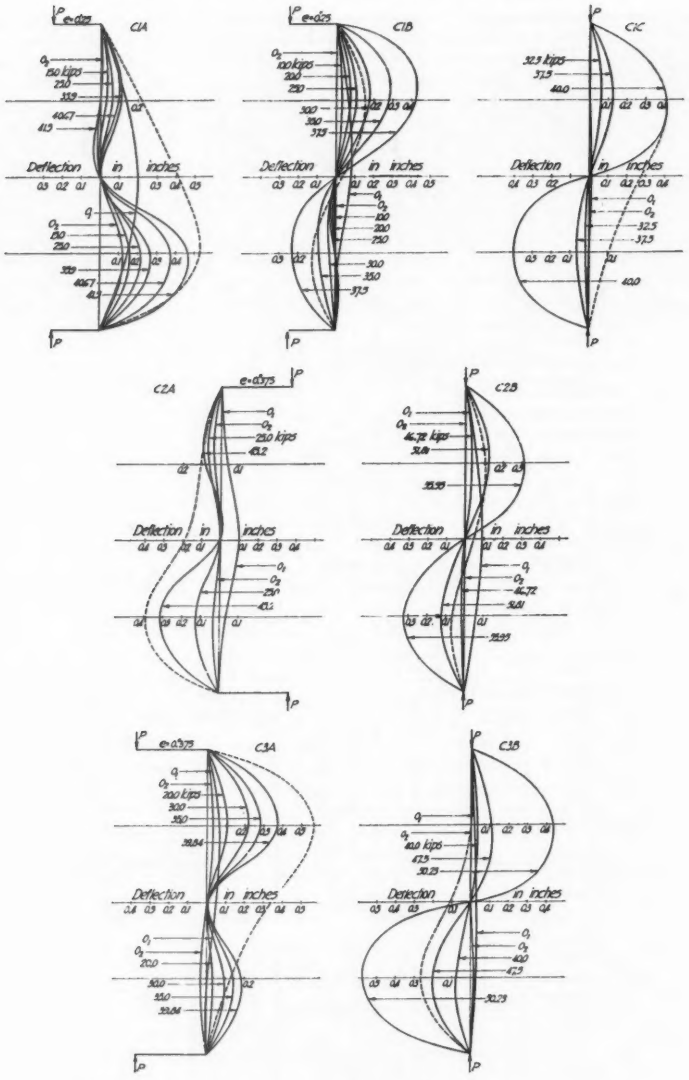
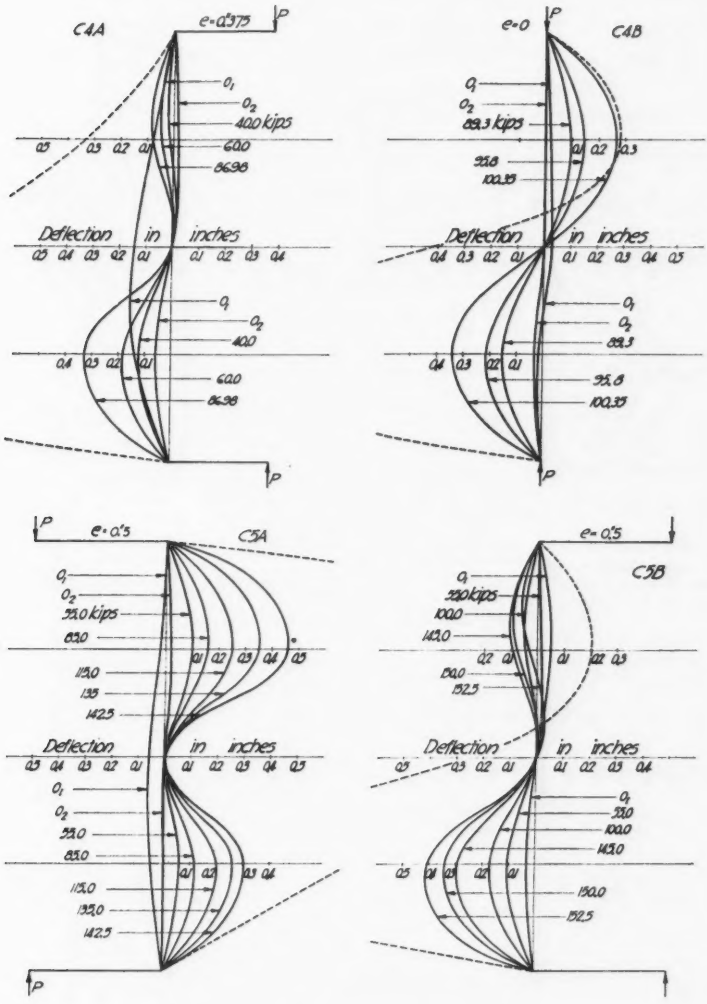


FIG. 8. *Observed relation of lateral force to axial load for columns C1A to C4B to maintain zero deflection at point of support.*



NOTE :-
The axial load corresponding to each deflection curve is indicated in kips.
Q_1 indicates the form of the unloaded column.
Q_2 indicates the form of the column under zero axial load, when the mid-point of the flange is forced to lie on the line joining the ends of the column shaft.
The broken line indicates permanent deformation.

FIG. 9. *Observed deflections of East flange of columns C1A, C1B, C1C, C2A, C2B, C3A, and C3B for mid-height deflection of zero at East flange.*



NOTE :-

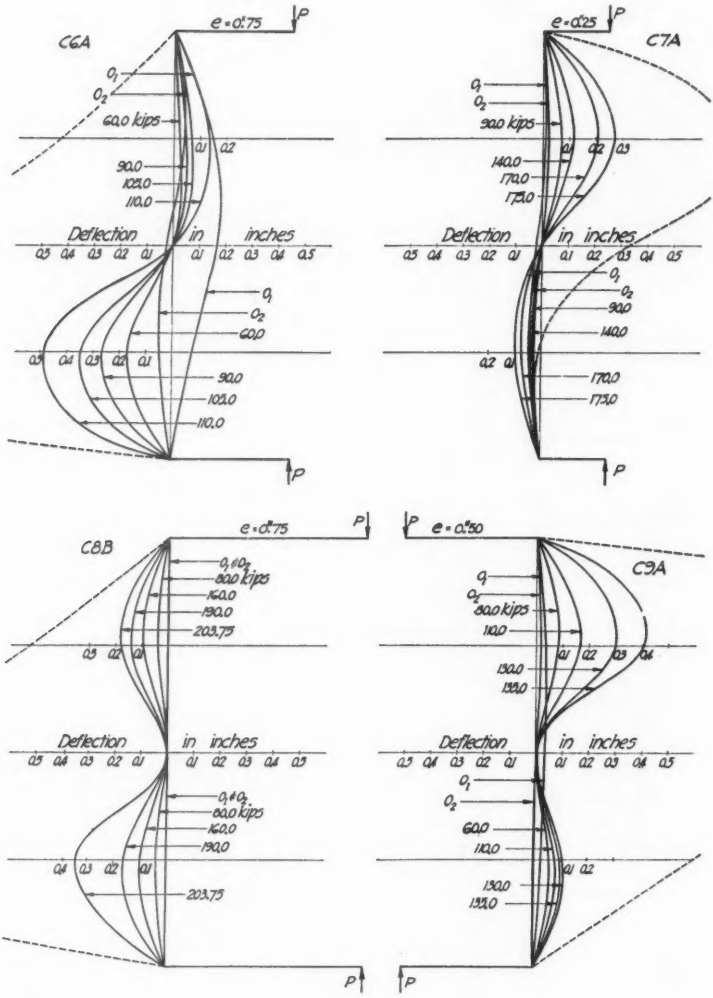
The axial load corresponding to each deflection curve is indicated in kips.

O_1 indicates the form of the unloaded column.

O_2 indicates the form of the column under zero axial load, when the mid-point of the flange is forced to lie on the line joining the ends of the column shaft.

The broken line indicates permanent deformation.

FIG. 10. *Observed deflections of East flange of columns C4A, C4B, C5A, and C5B for mid-height deflection of zero at East flange.*



NOTE -

The axial load corresponding to each deflection curve is indicated in kips.

O_1 indicates the form of the unloaded column.

O_2 indicates the form of the column under zero axial load, when the mid-point of the web is forced to lie on the line joining the ends of the column shaft.

The broken line indicates permanent deformation.

FIG. 11. *Mean deflections of flanges of columns C6A, C7A, C8B, and C9A for mid-height deflection of zero at middle of web.*

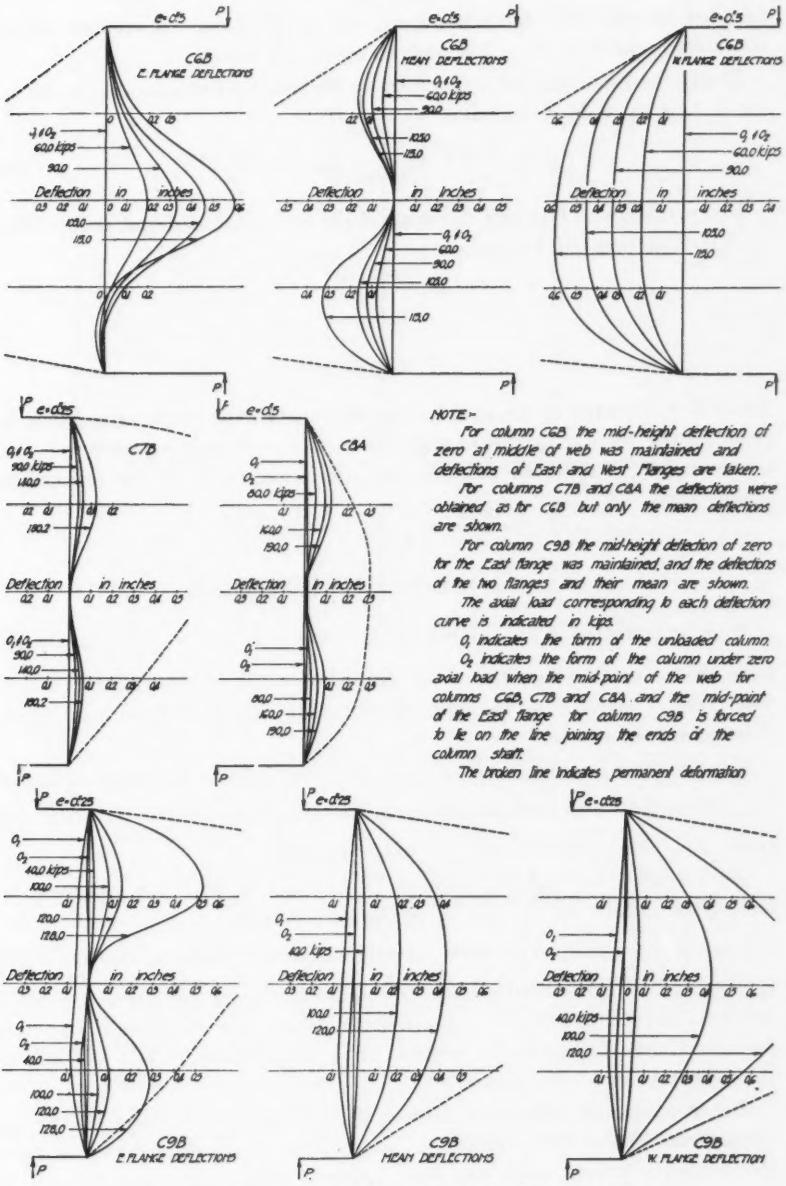


FIG. 12. *Deflections of columns C6B, C7B, C8A, and C9B.*

adapted to take into account natural or initial crook. A column will be considered with a crook, c, but with no accidental errors.

Modifying Equation (18) to conform to the results of experiment, by replacing $1.23\ e$ by $1.33\ e$, we have

$$Q = \frac{4.87P}{l}(\Delta + 1.33e) - \frac{48EIn}{l^3}. \tag{20}$$

It is necessary to find first the slope of the zero axial load line, 0–0. When $P = 0$, Equation (20) becomes

$$Q = \frac{48EIn}{l^3}.$$

If now

$$n = \frac{l}{4.87X},$$

where X = the ratio of the axial load as indicated by the height of any selected point on the vertical axial load scale to the lateral supporting force indicated by the height of the same point on the lateral load scale, or the ratio of the scales, then

$$Q = \frac{48EI}{l^3} \times \frac{l}{4.87X} = \frac{1}{X} \cdot \frac{\pi^2 EI}{l^2}$$

$$= \frac{1}{X} \times \text{Euler load for the column.}$$

Now, as indicated in Fig. 13, lay off $O'A = n = \Delta - c = \frac{l}{4.87X}$ to the left from the point O' where $OO' = c$, the initial crook of the column, if any. The point O' may be to the right or left of the origin O, depending on the direction of the crook.

From A erect a vertical AB equal to the Euler load on the axial load scale, or $\frac{1}{X}$ times the Euler load, according to the lateral force scale. Join BO' and produce. This gives 0–0, the zero axial load line.

Next, erect a vertical $O'C$ through O' and lay off on it the various axial loads to be considered, e.g., $O'C = 60{,}000$ lb. Join BC.

Lay off $\Delta = OD = \frac{4}{3}e$ from the original vertical axis, to the left if the eccentricity is to the South, or to the right, if it is to the North. Erect a vertical DE cutting 0–0 at E. E will be the point of intersection of load lines for an eccentricity of e to the South. Draw EF parallel to BC. EF will be the 60,000 lb. load line.

For any assumed deflection Δ from the vertical axis through O, that is, through the ends of the column, the corresponding vertical height to EF gives the necessary lateral supporting force applied symmetrically to the width of the column, or what has been called web support. For example, for a deflection of OG to the North, the lateral supporting force is GW.

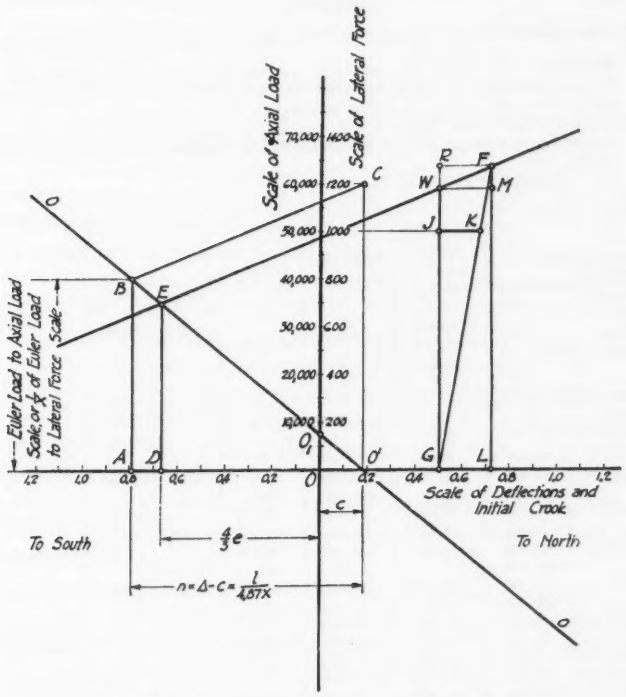


FIG. 13. *Construction of Jackson diagram.*

If the column were supported on the edge of a flange, the lateral force necessary to hold the flange to a deflection of OG will be increased. The method of determining this lateral force for flange support and for a flange deflection of, say, OG is as follows:

Estimate from the known torsional characteristics of the section considered the amount of torsional displacement Δ_t of a flange under an applied load Q_f = 1000 lb. at the edge of the flange and in its plane. Lay off GJ = 1000 lb. and $JK = \Delta_t$. Produce GK to F. Then, the height LF gives the lateral support required for a deflection $\Delta = OG$ of the supported flange if the support is at the flange edge. Its excess over the required web support is MF.

13. Value of Lateral Support

Table II indicates the increase in ultimate strength of a hinged column laterally supported at mid-height without applied rotational restraint over the strength of a corresponding column without intermediate lateral support of any kind.

The ultimate test load of each column is compared with *(a)* the theoretical Euler load for zero eccentricity, Equation (1), based on a length of 240 in.,

TABLE II

RELATION OF OBSERVED ULTIMATE STRENGTH OF THE TEST COLUMNS TO THEORETICAL STRENGTH

NOTES: (1) Eccentricity of loading was in every case normal to the plane of the web. N = North eccentricity, that is, the axial load was applied to the North of the gravity axis of the column. S = South eccentricity.
(2) Ultimate loads were applied with the lateral support at the edge of one flange, except for specimen *C9A*, for which the lateral support was provided at the centre of the web.
(3) E = 29,000,000 lb. per sq. in.

Column mark	Eccentricity of ultimate test load at end of column, in.	Ultimate test load, lb.	Theoretical ultimate load by Formula (21) for full-length crooked column, lb.	Theoretical Euler load (zero ecc'y) for l = 240 in., lb.	Slenderness ratio $\frac{l}{r}$ for l = 240 in.	Ratio of (3) to (5)	Ratio of (3) to (4)	Remarks
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	
C1A	0.25 S	42,000	8,620	9,840	353	4.27	4.87	Continuity moment
C1B	0.25 S	35,490	9,350	10,350	353	3.43	3.80	
C1C	0	40,200		10,060	353	3.99		
C2A	0.375 S	48,050	13,690	15,500	324.3	3.10	3.51	Continuity moment
C2B	0	52,800	14,100	14,680	324.3	3.59	3.75	
C3A	0.375 S	47,700	11,700	13,440	303.9	3.55	4.07	Continuity moment
C3B	0	50,400		13,440	303.9	3.75		
C4A	0.375 N	98,900	22,100	26,610	272.9	3.71	4.47	Continuity moment
C4B	0	101,000		26,610	272.9	3.79		
C5A	0.50 S	145,000	36,900	45,000	237.7	3.22	3.93	Continuity moment
C5B	0.50 N	152,500	37,200	45,300	237.7	3.37	4.10	Continuity moment
C6A	0.45 N	110,500	34,200	39,800	208.7	2.78	3.23	
C6B	0.56 N	116,200	30,200	38,850	208.7	3.02	3.84	Continuity moment
C7A	0.25 N	178,200	60,000	71,000	184.6	2.51	2.97	
C7B	0.23 S	180,200	60,800	70,300	184.6	2.56	2.96	Continuity moment
C8A	0.53 S	207,000	72,600	102,800	156.9	2.02	2.85	Continuity moment
C8B	0.77 N	203,750	65,800	102,800	156.9	1.98	3.10	Continuity moment
C9A	0.50 S	139,500	41,600	54,400	206.9	2.56	3.35	Continuity moment
C9B	0.25 S	129,100	47,800	53,200	206.9	2.43	2.70	Continuity moment

the distance between the end pivots, and *(b)* the theoretical ultimate load by the commonly employed secant formula

$$P = A \cdot \frac{f_y}{1 + \frac{ey_1}{r^2} \sec \frac{l}{2}\sqrt{\frac{P}{EI}}}, \qquad (21)$$

in which f_y = compressive yield point of the steel, taken for all columns as 36,000 lb. per sq. in.;
e = eccentricity of load with respect to the column axis at mid-height, that is, including the effect of crook;
y_1 = distance from column axis to extreme fibre of column section in the plane of bending;
r = radius of gyration;
l = theoretical length of column;
E = modulus of elasticity of the material;
I = moment of inertia of the column in the direction of bending.

Three major influences affect the extent of the improvement in strength: *(a)* the slenderness ratio of the column; *(b)* the eccentricity of the loading; and *(c)* the existence of continuity moment at mid-height.

With equal eccentricities of the same sign at the two ends the column tends to bend in the same direction in the upper and lower halves and thus to develop continuity moment at the middle support. This was found to exist in most eccentrically loaded columns, as is apparent in Table II. But, doubtless owing to some accidental and unpredictable irregularities, the bending was opposite in sense in the two halves for columns *C1B*, *C6A*, and *C7A*. With zero eccentricity the nature of the buckling is unpredictable. Figs. 9 to 12, inclusive, show the form of the bending.

In column (7) of Table II is indicated the ratio of the ultimate test load to the theoretical Euler load calculated on the assumption that no intermediate lateral support existed. This ratio varies from 1.98 for specimen *C8B*, which is one of those having the lowest slenderness ratio, to 4.27 for *C1A*, which is one of those having the highest slenderness ratio. The eccentricity for the first-mentioned column was larger than that for any of the other columns, and for the last-mentioned it is one of the smallest for the eccentrically loaded columns. Continuity moment at mid-height existed for both of these extreme cases.

While the load stages were based on the Euler load and a comparison of the ultimate test load with it has been made, it is obvious that the calculated Euler load has but slight significance for columns with eccentricity of loading. Comparison of the test load with the ultimate load computed by the secant formula is, however, valid.

Column (8) of Table II indicates that the ultimate test load related to the ultimate load as calculated by the secant formula gave ratios ranging from 2.7 for column *C9B* to 4.87 for column *C1A*. The slenderness ratio ranged, respectively, from the third lowest value to the highest value. The eccentricities were the same and continuity moment existed in both cases.

Table II indicates that, as might be expected, the benefit of lateral support tends to be least for columns having the lowest values of the slenderness ratio. There appears to be no clear-cut and consistent law discernible from the tests respecting the relation of the benefit of lateral support to the eccentricity.

It is, however, useful to know that for columns with eccentricity up to one-eighth of the column width the furnishing of lateral support at mid-height of the column increases the strength to from 2.70 to 4.87 times the theoretical strength of the full-length column as computed by the secant formula.

14. Recommended Values for the Lateral Supporting Force for Web Support

Examination of the relation of the experimental lateral-force–deflection lines to the plotted theoretical points for all the columns showed that the plotted points for the approximate formulae of Equations (18) and (19), for the so-called exact formulae of Equations (7) and (17), and for the Jackson diagram conform fairly well to the experimental curves, except in the cases of

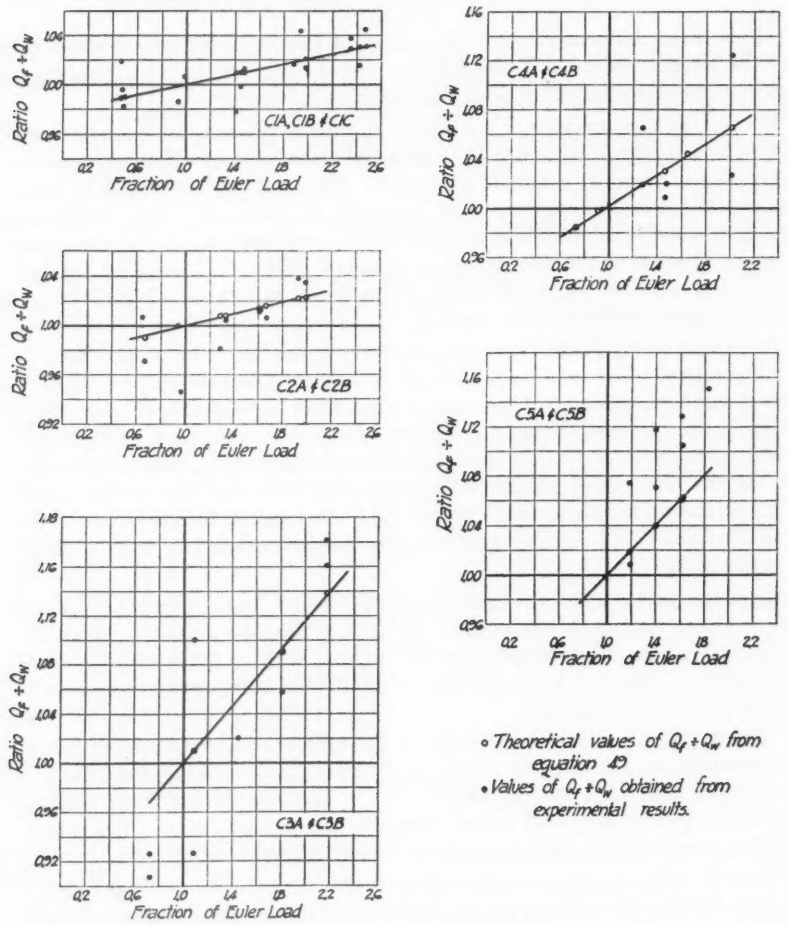


FIG. 14. *Comparison of theoretical and experimental values of the ratio* $Q_f \div Q_w$.

the larger axial loadings. As is evident from Fig. 8, the ratio that the lateral force Q bears to the axial load P to maintain zero deflection at the point of support increases somewhat with the load. There is no reason to suppose that the variation would be markedly different if some deflection were permitted at the point of support.

Various adjustments of the proposed formulae for the value of the lateral supporting force were tried in order to give greater weight to the magnitude of the axial force, some involving exponential functions. On the whole, the most satisfactory one resulted from a slight modification of Equation (20),

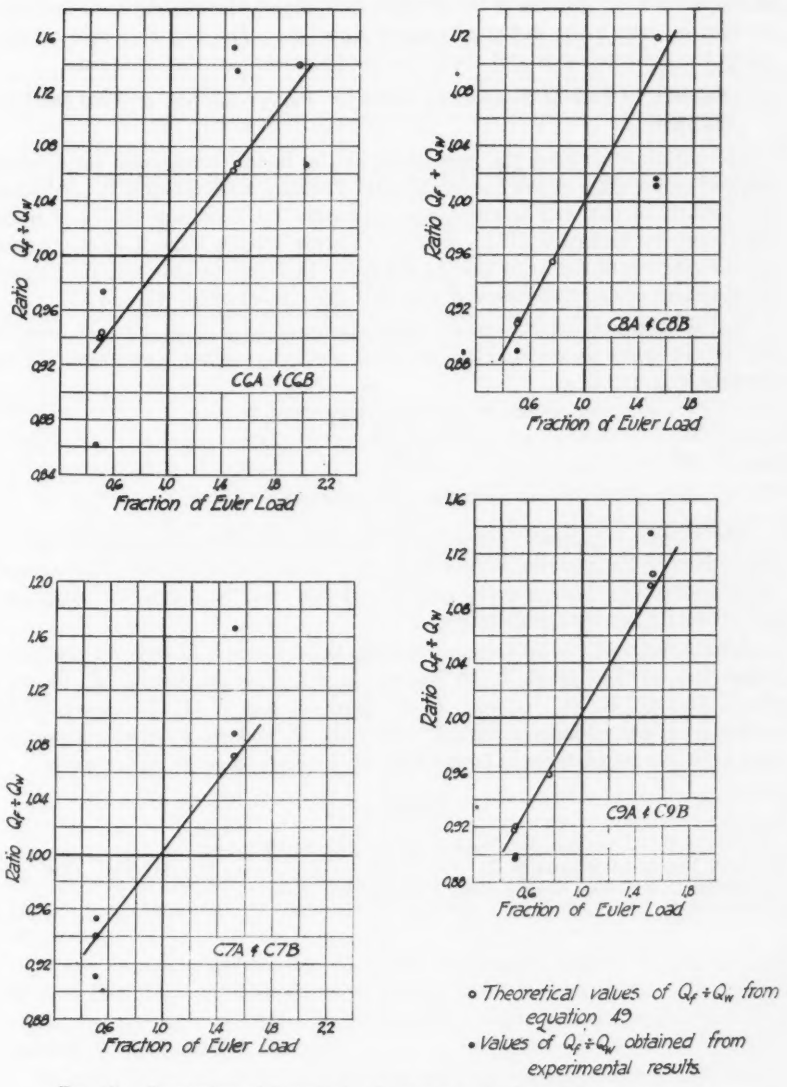


FIG. 15. *Comparison of theoretical and experimental values of the ratio* $Q_f \div Q_w$.

giving as the recommended working formula for the lateral supporting force, where the support is at the middle of the width of the section,

$$Q_w = \frac{5P}{l}(\Delta \pm 1.33e) - \frac{48EIn}{l^3} \qquad (22)$$

The plus sign is to be used in the first term of Equation (22) when the end eccentricity is on the side of the straight line joining the column ends opposite to that on which the deflected column axis lies. The negative sign applies when the deflected axis and the end eccentricity are on the same side.

15. Relation of Lateral Supporting Force for Flange Support to That for Web Support

The relation between the magnitude of the lateral supporting force when applied at the edge of the flange and the necessary force when it is applied at the middle of the web is given approximately by Equation (19) and more rigorously by Equation (17). The ratios given by the latter formula, based on the relation of the axial load to the Euler load for the column, are plotted on diagrams giving the observed values of the ratios in Figs. 14 and 15.

A simplified variant of Equation (19) was found to give results that were on the whole quite as satisfactory as those given by either Equation (19) or Equation (17). It is

$$Q_f = \frac{Q_w}{1 + \frac{h^2 l}{E_s J}\left(\frac{3EI}{l^3} - \frac{P}{3l}\right)}. \qquad (23)$$

Acknowledgments

The authors are greatly indebted to the National Research Council and to the School of Engineering Research of the University of Toronto for financial assistance received in connection with the work. Without this, the investigation would have been impossible.

Acknowledgment is here made (in alphabetical order) of the able and conscientious services of R. I. P. Barnes, H. St. Paul Butler, C. E. Helwig, G. V. Helwig, K. B. Jackson, P. V. Jermyn, and C. F. Morrison. The authors are particularly indebted to Prof. K. B. Jackson for many ingenious and valuable suggestions in connection with various aspects of the work.

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THE ISOLATION OF CICUTIN FROM *CICUTA MACULATA* L.[1]

BY LÉO MARION[2]

Abstract

One of the constituents of the root of *Cicuta maculata* L. has been isolated in crystalline form. It has been found to contain three methoxyl groups and to possess a lactone structure.

The designation water hemlock has been applied indiscriminately to many species of the genus *Cicuta* (Umbelliferae) such as *C. vagans*, *C. occidentalis*, *C. virosa*, and *C. maculata*. The resinous, ether soluble products obtained from several of these plants have all been named cicutoxin, with the consequent implication that they are identical (1, 2, 4). It has long been known that a deadly poison is contained in the root of some species of *Cicuta* and that the resinous product possesses the toxic properties of the plant. *C. maculata* does not seem to have been investigated to the same extent as *C. occidentalis* or *C. virosa* although it is known to be poisonous. The toxicological studies, however, have yielded conflicting results, possibly because the species used was not always the same. Furthermore, the chemical knowledge extant, being based on experiments carried out with an amorphous material and not with a homogeneous substance, cannot be taken as definite.

Cicutoxin has been investigated chemically by Jacobson (2), by Schneider and Kotrba (5), and by Svagr (8). Jacobson, who isolated his cicutoxin from *C. occidentalis*, described it as a yellowish, viscous resin polymerizing spontaneously to a semisolid body of a ruby-red to reddish-brown colour. From an analysis of this resin Jacobson suggested the empirical formula $C_{19}H_{26}O_3$ for cicutoxin to which, on the basis of scanty evidence, he assigned a γ-pyrone structure.

In the course of the last twelve years, numerous complex coumarins have been isolated from various plants belonging to the Umbelliferae. It appeared, therefore, probable that the water hemlock might contain compounds possessing the coumarinic structure.

The root of *C. maculata* was extracted with petroleum ether and the extract, after separation of the fat and fatty acids, yielded a substance which could be crystallized from ether or methanol. In order to avoid ambiguity, it is

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proposed to designate this substance by the name cicutin. Crystalline cicutin yielded analytical figures in good agreement with the empirical formula $C_{22}H_{22}O_7$, and it has been found to contain three methoxyl groups. It was found to be insoluble in aqueous sodium carbonate, but soluble in sodium hydroxide. When treated with sodium hydroxide and dimethyl sulphate it gave rise to an ester-ether which, on saponification, produced an acid containing four methoxyl groups. Diazomethane, however, failed to react. Furthermore, when cicutin was dissolved in standard sodium hydroxide and the solution titrated with standard hydrochloric acid, a potentiometric curve (Fig. 1) was obtained which exhibits two horizontal sections, each correspond-

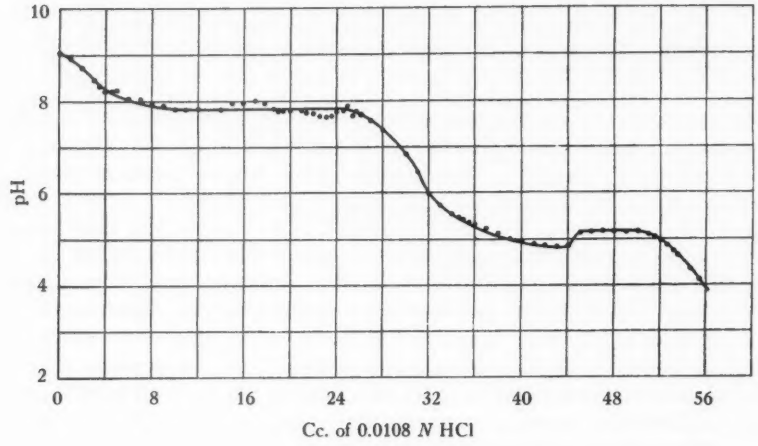

FIG. 1.

ing to a group in the molecule which combined with sodium hydroxide. The foregoing facts indicate a lactone structure. Of the seven atoms of oxygen present in cicutin, five are accounted for by the three methoxyl groups and the lactone ring. Neither of the two remaining oxygen atoms seems to be part of a furan ring since all attempts to oxidize cicutin with hydrogen peroxide according to the procedure used by Späth and v. Christiani (6) have so far failed to produce furan-2 : 3-dicarboxylic acid. Further than this, no insight into the constitution of cicutin has been obtained.

Dr. C. A. Morrell, pharmacologist of the Department of Pensions and National Health, Ottawa, kindly undertook to determine the toxicity of the crude extract and of pure cicutin, and the author takes this opportunity to acknowledge his indebtedness. The residue from the petroleum ether extract of the root, dissolved in 20% alcohol, was found to be toxic to frogs and to cause the same symptoms as described by earlier investigators (3). No toxicity, however, was observed towards guinea pigs. Unfortunately, it was

not possible to determine whether the same toxicity could be attributed to crystalline cicutin, owing to its insolubility in dilute alcohol or in any of the suitable solvents.

Experimental

Isolation of Cicutin

The plant material utilized for this work was collected in the vicinity of Ottawa and kindly identified by Dr. H. Senn, Botanist at the Dominion Experimental Farm, Ottawa, as *Cicuta maculata* L. The cleaned roots, air-dried and ground, weighed 11.4 kilos. They were extracted in Soxhlets with petroleum ether and the solvent was removed by distillation from the combined extracts. After standing for several days, the oily residue had deposited a crystalline solid which was filtered (Filtrate *A*) through a fritted glass funnel. The crystalline solid was dissolved in methanol (200 cc.), added to a solution of sodium hydroxide (40 gm.) in methanol (200 cc.), and allowed to stand at room temperature for five hours, with frequent shaking. At the conclusion of this treatment, the methanol was distilled under reduced pressure, water (2 litres) added to the residue, the mixture stirred, and allowed to stand overnight. Next day a sludge had settled to the bottom, and the clear supernatant liquor was siphoned off and filtered through a layer of Celite. Water was added to the sludge, which was stirred and allowed to settle, and the supernatant liquor was siphoned off, and filtered. The combined filtrates were acidified with hydrochloric acid, allowed to stand several hours, and extracted repeatedly with ether. During this extraction, a crystalline solid separated which was filtered off, washed with ether, and recrystallized repeatedly from methanol. It was obtained finally as soft colourless needles, m.p. 171°.*

The combined ether extracts still contained free fatty acids, and in order to remove these the ether solution was placed in a separatory funnel and 0.5% aqueous sodium hydroxide (2 litres) was run, drop by drop, into the funnel, the aqueous layer being drawn off from time to time. The ether layer was afterwards washed with water, dried over sodium chloride, and distilled. A crystalline residue weighing 17 gm. was left, which when recrystallized from a mixture of methanol and ether melted at 168° C. After several recrystallizations from methanol, it separated as soft needles, m.p. 171°, identical with the substance obtained above. Calc. for $C_{22}H_{22}O_7$: C, 66.33; H, 5.53; 3 OCH_3, 23.36%; mol. wt. 398. Found: C, 66.29, 66.49; H, 5.45, 5.49; OCH_3, 23.22, 23.34%; mol. wt. (Rast), 358, 384.

The oily filtrate *A*, mentioned above, was dissolved in methanol (200 cc.), poured into a solution of sodium hydroxide (40 gm.) in methanol (200 cc.), and treated exactly as described in the case of the solid material. This yielded a further small quantity of cicutin. The total yield of purified cicutin amounted to 0.13% of the weight of the dried roots.

* *All melting points are corrected.*

Hydrolytic Methylation of Cicutin

Following the procedure described by Späth, Dey, and Tyray (7), cicutin (150 mg.) was dissolved in 3% aqueous sodium hydroxide (20 cc.) with the aid of heat. To this solution was added 10% sodium hydroxide (12.4 cc.) and freshly distilled dimethyl sulphate (3.3 cc.), and the mixture boiled under reflux for seven minutes. This treatment was repeated four times, the same quantities of 10% sodium hydroxide and dimethyl sulphate being added between the periods of heating. After the fifth heating, 10% aqueous sodium hydroxide (10 cc.) was added and the flask kept on the steam-bath for 10 min. to saponify the ester. The solution was cooled, acidified with 6*N* hydrochloric acid (10 cc.) and allowed to stand overnight. The white precipitate was collected in ether, extracted with three portions of 3% aqueous sodium bicarbonate (15 cc. each), washed with water, and dried over sodium chloride. Removal of the ether by distillation left a small residue of unchanged cicutin; m.p. 170° C. either alone or in admixture with an authentic sample. The combined sodium bicarbonate extracts were acidified with dilute (1 : 1) hydrochloric acid and the precipitated acid was collected in ether. The ethereal solution was washed with water, dried, and distilled to remove the solvent. The residue consisted of a crystalline acid which, after recrystallization from boiling methanol, melted at 194 to 195°. Yield, 80 mg. Calc. for $C_{23}H_{26}O_8$: 4 OCH_3, 28.84%. Found: OCH_3, 27.04%.

Potentiometric Titration of Cicutin

Cicutin (0.1096 gm.) was dissolved in 0.0092 *N* sodium hydroxide (60.0 cc.), the solution kept well stirred and 0.0108 *N* hydrochloric acid added in small quantities at a time. After each addition the equilibrium value of the pH was read on a Beckman pH meter. The results are plotted in Fig. 1. The distance along the abscissa from the origin of the first plateau to the end of the second corresponds to a quantity of sodium hydroxide equivalent to a molecular weight of 419 for cicutin. The molecular weight calculated for $C_{22}H_{22}O_7$ is 398.

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STUDIES ON DICYANOTRIAZOLE

I. THE CONDUCTANCE OF DILUTE AQUEOUS SOLUTIONS OF DICYANOTRIAZOLE AT 25° C.[1]

By E. G. Taylor[2]

Abstract

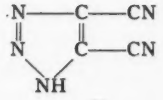
Previous experimental studies of dicyanotriazole have resulted in statements that the compound is an acid comparable in strength with the strong mineral acids.

In the present work, measurements of the equivalent conductance of dicyanotriazole in dilute aqueous solution give the dissociation constant of the acid as 3.378×10^{-3} at 25° C., thus showing it to be an acid possessing about the same strength as dichloracetic acid.

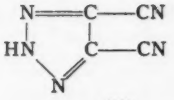
The limiting equivalent conductance of dicyanotriazole at 25° C. is 384.9. The earlier work gave a value of 397.44.

Introduction

In this laboratory a comprehensive investigation of the properties of dicyanotriazole has been undertaken. This substance was first obtained by Grishkevich-Trokhimovskii (6). Fialkoff (3) confirmed Trokhimovskii's observation that the dicyanotriazole existed in two crystalline modifications—a yellow form and a colourless form. The colourless form, to which Formula I was given, was obtained by sublimation of the yellow form (Formula II)



(I)



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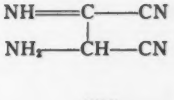


(III)

Hinkel and his co-workers (7) have shown that the yellow variety is merely an impure form of dicyanotriazole. These observations have been confirmed in the present work.

Fialkoff (3) states that dicyanotriazole is to be regarded as a strong acid comparable in strength with hydrochloric or nitric acid, but the published data do not permit an accurate calculation of the dissociation constant of the acid. In his paper he reports measurements of the electrical conductances of the supposed two varieties. The difference in the reported values is small (3 to 4%), and it becomes inappreciable at the higher concentrations investigated.

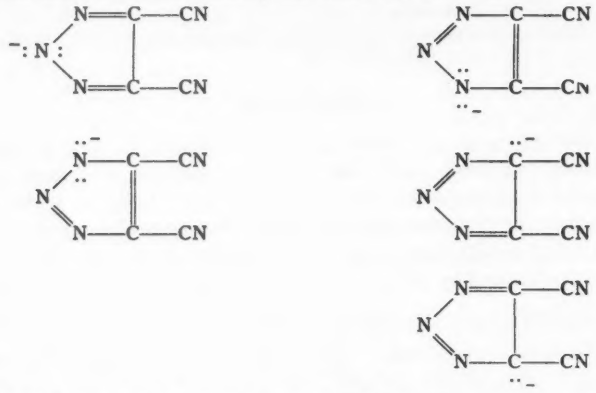
Using the results of conductance measurements on the sodium salt of dicyanotriazole, Fialkoff arrives at a Λ_0 value of 98.64 for this salt. Subtracting the mobility of the sodium ion, i.e., 51.2 at 25° C. (10), gives the mobility of the dicyanotriazole anion as 47.44. Finally taking the mobility

[1] *Manuscript received March 28, 1942.*
Contribution from the Chemical Laboratories, Queen's University, Kingston, Ont.

[2] *Lecturer in Chemistry.*

of the hydrogen ion as 350 he gives the Λ_0 value for dicyanotriazole as 397.44. Using this value of the limiting conductance, Fialkoff calculates the conductance ratios over the concentration range 0.002 to 0.4 *N*. These values vary from 0.87 in the dilute solutions to 0.25 in concentrated solution. It seems clear that dicyanotriazole is highly dissociated in dilute aqueous solution —much more so than most organic acids.

A study of the formula of dicyanotriazole reveals an interesting situation. The anion formed by ionization of the dicyanotriazole exhibits lack of saturation of the atomic valencies. To explain the apparent stability of the anion of dicyanotriazole, the concept of quantum mechanical resonance must be used. The anion resonates among the following five structures:



and hence the molecule is made unstable relative to the anion. In addition the ionic character of the triple bond of the cyanide group (13, p. 184) assists in stabilizing the structure of the anion. It is clear therefore that dicyanotriazole may be a relatively strong acid, particularly in aqueous solution.

In this paper, measurements of the conductance of dicyanotriazole in aqueous solution at 25° C. over the concentration range 2×10^{-4} to 8×10^{-3} *N* are reported. An accurate value of the dissociation constant has been calculated and the mobility of the anion of dicyanotriazole obtained.

Experimental

Apparatus

Conductance measurements were made with an accurate a-c. direct reading type of bridge built in accordance with modern specifications. A variable frequency oscillator (600 to 3000 cycles) provided the alternating current while a pair of telephones in conjunction with a simple pentode amplifier served as detector. The conductance cell was of the Erlenmeyer type described by Cox, Kraus, and Fuoss (1). The electrodes were lightly platinized. The cell constant was 1.280—determined by intercomparison with a cell the constant of which was 4.873. The constant of the latter cell was determined using Jones and Bradshaw's data (8) for 0.01 demal potassium chloride

solution at 25° C. The cell capacitance was negligible and measurements of resistances were made at 600, 1000, and 2000 cycles. Polarization corrections were applied when necessary (9). An oil thermostat controlled by a thyratron tube maintained a temperature of 25.00° C. (± 0.02° C.).

Materials

Conductance water was prepared by fractional condensation of steam in an all-Pyrex still in a current of air freed from carbon dioxide and ammonia.

Preparation of Dicyanotriazole

Pure hydrogen cyanide was prepared by the usual method of dropping saturated sodium cyanide solution into 50% sulphuric acid solution heated to 80° C. The liquid hydrogen cyanide was dried by shaking with anhydrous sodium sulphate. To the dried liquid about 3% of its weight of sodium cyanide was added. On standing for 24 to 48 hr. in a closed vessel the whole mass underwent a violent reaction, resulting in the production of a black coal-like mass.

The black material was extracted with ether in a Soxhlet apparatus. The ether solution on evaporation yielded a dark brown crystalline substance, which has been shown to be iminoaminosuccinonitrile (7), Formula III. The yield was about 3%, based on the hydrogen cyanide used.

The crude brown product was suspended in water and diazotized with sodium nitrite solution and hydrochloric acid. After careful diazotization at a temperature below 10° C. the solution was heated to 90° on a steam-bath and treated with Norit. The mixture was then filtered and the cold colourless filtrate extracted several times with ether. On evaporation of the ether, white crystalline dicyanotriazole remained (7). The dicyanotriazole was crystallized repeatedly from ethylene dichloride and finally dried over phosphorus pentoxide *in vacuo*. As a test of its purity, conductance measurements were made with samples that had been crystallized different numbers of times. Agreement between the electrical measurements is an excellent criterion of purity. The melting point of the dicyanotriazole was 148° C. (corrected).

Method

All solutions were made up by a weight dilution method (11). About 100 mg. of the acid was weighed out into the conductance cell and about 150 gm. of conductance water weighed into the cell. The cell was placed in the thermostat and the resistance measured when temperature equilibrium was attained. The cell was then removed from the thermostat, wiped clean of oil, and about half the solution removed by means of an evacuated weight pipette provided with a long capillary tip. The solution removed was replaced by conductance water and after weighing again another resistance measurement was made. This procedure was repeated five or six times for each run.

In all cases the measured resistances were perfectly constant and did not vary with time, even over long periods.

Volume concentrations were calculated on the assumption that the densities of the solution were the same as the density of the pure solvent. No correction was made for the conductance of the water.

Results

The experimental results are summarized in Table I. Three independent runs were carried out. A plot of Λ against $\sqrt{c}$ is shown in Fig. 1.

TABLE I

THE CONDUCTANCE OF DICYANOTRIAZOLE IN WATER AT 25° C.

Concentration, $c \times 10^4$	Equivalent conductance, Λ	Concentration, $c \times 10^4$	Equivalent conductance, Λ
(a) Specific conductance of water $= 8 \times 10^{-7}$ *r.o.*			
82.85	317.7	9.215	371.2
50.42	336.2	4.175	376.6
31.70	349.8	2.056	377.2
19.54	360.7		
(b) Specific conductance of water $= 1.0 \times 10^{-6}$ *r.o.*			
47.50	338.8	6.901	373.8
27.17	354.2	2.871	377.0
12.82	367.6		
(c) Specific conductance of water $= 1.0 \times 10^{-6}$ *r.o.*			
58.49	331.2	11.18	368.7
29.32	352.2	4.665	375.3
18.70	361.3	2.100	375.8

Discussion

It is impossible to obtain the Λ_0 value for dicyanotriazole by extrapolation of the $\Lambda/\sqrt{c}$ plot, since its slope is considerably greater than that predicted by the Onsager equation (12). Furthermore, the Λ values are not reliable at concentrations less than 4×10^{-4} N, probably because of a reaction between impurities in the water and the dicyanotriazole.

To obtain the Λ_0 value and the true thermodynamic dissociation constant of dicyanotriazole, recourse is made to the limiting laws that have been developed on the basis of Coulombic interaction between the ions. These are the following:

$$\Lambda = \gamma(\Lambda_0 - \alpha\sqrt{c\gamma}), \quad (5)$$

where γ satisfies the ordinary mass law equation

$$\frac{c\gamma^2 f^2}{1 - \gamma} = K,$$

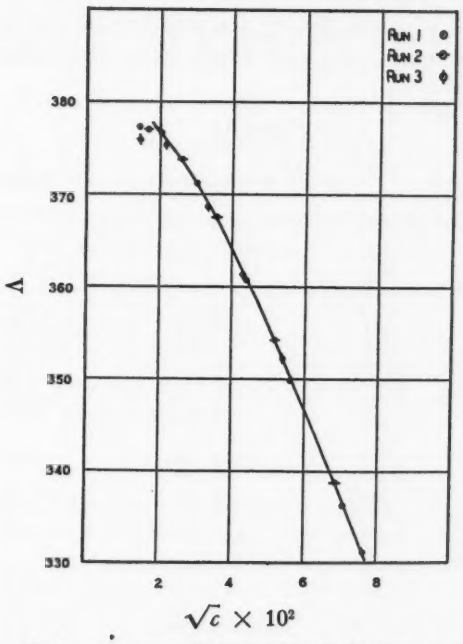


FIG. 1. *Conductance curve of dicyanotriazole in water at 25° C.*

and f is given by the Debye–Hückel limiting equation (2)

$$-\log f = \beta\sqrt{c\gamma},$$

Λ = equivalent conductance at concentration C (gram-equivalents per litre of solution),
Λ_0 = limiting conductance,
γ = fraction of solute dissociated,
f = activity coefficient,
α = Onsager's coefficient (12),
β = Debye and Hückels' constant,
K = dissociation constant.

Fuoss (4) has introduced a function $F(z)$, where $z = \alpha\Lambda_0^{-\frac{3}{2}}\sqrt{c\Lambda}$, thereby obtaining the relation between equivalent conductance and concentration in the form of a straight line. This final equation is

$$\frac{F(z)}{\Lambda} = \frac{1}{K\Lambda_0^2}\,\frac{C\Lambda f^2}{F(z)} + \frac{1}{\Lambda_0}.$$

The values of $\frac{F(z)}{\Lambda}$ and $\frac{c\Lambda f^2}{F(z)}$ for dicyanotriazole are given in Table II. The third column of Table II gives the percentage deviation

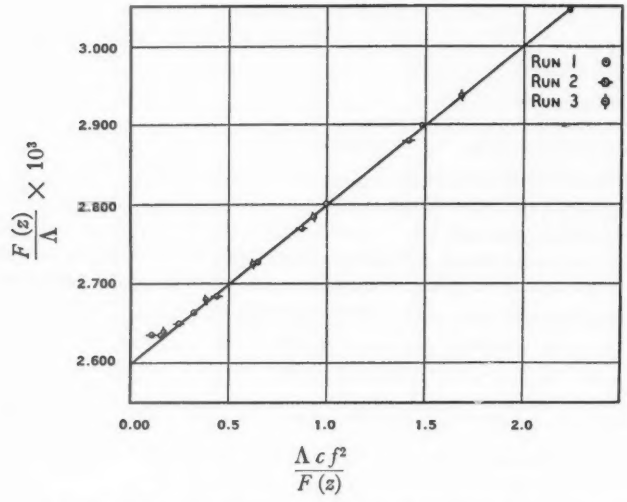
$$\Delta = \left\{\left(\frac{F(z)}{\Lambda}\right)_{interpol.} - \left(\frac{F(z)}{\Lambda}\right)_{obs.}\right\} 100\left(\frac{\Lambda}{F(z)}\right)_{interpol.}$$

when a straight line is drawn through the experimental points. When the deviation is positive $\Lambda_{obs.} > \Lambda_{interpol.}$ Fig. 2 shows the straight line relation between $\frac{c\Lambda f^2}{F(z)}$ and $\frac{F(z)}{\Lambda}$.

TABLE II

CALCULATED VALUES OF $\frac{F(z)}{\Lambda}$ AND $\frac{c\Lambda f^2}{F(z)}$ FOR DICYANOTRIAZOLE IN WATER AT 25° C.

	$\frac{c\Lambda f^2}{F(z)}$	$\frac{F(z)}{\Lambda} \times 10^3$	Δ
(*a*)	2.237	3.045	−0.00
	1.487	2.898	−0.10
	0.9979	2.800	−0.09
	0.6479	2.727	−0.00
	0.3227	2.663	−0.00
	0.1511	2.634	−0.14
(*b*)	1.417	2.878	+0.09
	0.8724	2.769	+0.11
	0.4400	2.683	+0.11
	0.2452	2.649	−0.09
	0.1048	2.635	−0.57
(*c*)	1.685	2.936	−0.07
	0.9326	2.783	+0.05
	0.6222	2.724	−0.04
	0.3866	2.678	−0.15
	0.1682	2.638	−0.23



Test of the Fuoss conductance function for dicyanotriazole in water at 25° C.

The agreement with the linear relation is seen to be good, except for one or two points for very dilute solutions. The intercept of the straight line on the $\frac{F(z)}{\Lambda}$ axis is 0.002598, giving a value of 384.9 for Λ_0. The slope of the line, equal to $\frac{1}{K\Lambda_0^2}$, is 0.0001998, which yields a value of 3.378×10^{-2} for the dissociation constant of dicyanotriazole.

The mobility of the hydrogen ion at 25° C. is 349.72 (10), and therefore the mobility of the dicyanotriazole anion is 35.2.

It appears that dicyanotriazole is a relatively strong acid comparable in strength with dichloracetic acid for which $K = 5.14 \times 10^{-2}$. It is interesting that the value for the anion mobility is close to that for the propionate anion—34.3—which contains 10 atoms compared with 9 for the dicyanotriazole anion. The value obtained by Fialkoff—47.44 (3)—appears much too high for an anion of this nature.

Acknowledgment

Thanks are due to the Science Research Committee of Queen's University for financial assistance in purchasing apparatus and for providing the assistance of Mr. A. H. Haley, who carried out the lengthy preparation of the tetrapolymer of hydrogen cyanide.

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THE HYDROLYSIS OF PROPIONITRILE IN CONCENTRATED SOLUTIONS OF MINERAL ACIDS[1]

By J. D. McLean[2], B. S. Rabinovitch[3], and C. A. Winkler[4]

Abstract

The study of the hydrolysis of propionitrile in concentrated acid solutions has been extended to hydrobromic, nitric, and sulphuric acids for a range of acid concentrations. For the system of irreversible, unimolecular consecutive reactions, nitrile $\xrightarrow{k_1}$ amide $\xrightarrow{k_2}$ acid, $k_1 \ll k_2$ for all acid concentrations below 4 *N*. At higher concentrations, k_1 and k_2 are of the same order, and, in the case of sulphuric acid, k_1 becomes $\gg k_2$ at concentrations above 20 *N*. The observed activation energy decreases with increasing acid concentration for all acids. The specific differences in rate increase with acid concentration may be accounted for by the specific variations of *A* and *E* for each acid.

Introduction

In a previous investigation (4) of the hydrolysis of propionitrile in hydrochloric acid solutions from 0.5 to 10 *N*, it was shown that the system, nitrile $\xrightarrow{k_1}$ amide $\xrightarrow{k_2}$ acid, provides an example of unimolecular irreversible consecutive reactions over the complete range $k_1 \ll k_2$ (less than 4 *N*) to $k_1 \gg k_2$ (estimated above 11 *N*). This behaviour is contrary to a recent report (3) on the subject. A large decrease in activation energy of 6.7 Cal. over the range 1 to 10 *N* accounted in large measure for the marked increase in rate with acid concentration.

It was of interest to ascertain if the behaviour observed with hydrochloric is typical for mineral acids, and the investigation has therefore been extended to include sulphuric, nitric, and hydrobromic acids. At the same time, the parameters of the Arrhenius equation have been evaluated for each acid, over a range of concentrations, in a further effort to assess the importance of these factors for reactions in concentrated media.

Materials and Procedure

The acid solutions were prepared by dilution of reagent grade acids, standardized by both density and titration measurements.

Purification of propionitrile and preparation of its solutions were carried out as described previously (4).

Temperature was regulated to within 0.1° C., and measured with standard thermometers.

Krieble and Noll (3) have indicated that for sulphuric and hydrobromic acids, at concentrations comparable with those employed here, the hydrolysis

[1] *Manuscript received in original form February 4, 1942, and as revised, April 25, 1942. Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Que.*

[2] *Demonstrator in Chemistry.*

[3] *Holder of a Studentship under the National Research Council of Canada.*

[4] *Assistant Professor of Chemistry.*

of simple aliphatic nitriles may be followed by estimation of ammonia, i.e., that hydrolysis of the intermediate amide proceeds at a much faster rate than that of nitrile. The results of the previous study with hydrochloric acid suggested, however, that at higher acid concentrations both ammonia and amide should be determined. In the present study, ammonia alone, and the total of amide and ammonia both have been determined to evaluate the relative velocities of the two consecutive reactions and the influence of the intermediate on the over-all rate. The analytical procedures were the same as for hydrochloric acid.

Results

Experimental conditions and velocity constants for each of the three acids are shown in Tables I and II. The limited number of acid concentrations employed is sufficient to show the trends of the reaction rates. It may be seen that for acid concentrations of 1 to 4 N, the rate of amide hydrolysis is much greater (k amide: k nitrile $> 100 : 1$) than that of the nitrile, for all acids. This is evident from the equivalence of the k values obtained for hydrobromic acid by the two analytical methods, and also from the good constants obtained for nitric and sulphuric acids where analysis for ammonia only was made. Thus, determination of ammonia alone is sufficient at the more dilute concentrations. At higher acid concentrations, analysis for ammonia indicates that the hydrolysis has an induction period, which is eliminated, however, when data for both amide and ammonia content are considered. At these concentrations, therefore, the rates of nitrile and amide hydrolysis are of the same order.

The relations between the nature of the induction periods and the relative rates of the consecutive reactions of nitrile and amide have been previously discussed in the work on hydrochloric acid. For hydrobromic acid at 7.68 N, the velocity of hydrolysis, as given by ammonia formation, approaches the true nitrile value. However, the induction period is very pronounced and the ratio, k amide: k nitrile, is therefore less than 10 : 1, and is probably about 3 : 1. Since the upper limit of hydrobromic acid concentration ordinarily available is restricted, the rate ratios of the two reactions in hydrobromic acid solutions apparently may vary from k (nitrile) $\ll k$ (amide) (less than 4 N) to k (nitrile) $\backsim k$ (amide) (about 8 N).

With 13.01 N nitric acid, the k values obtained by analysis for ammonia do not approach the true nitrile rate, but level off at a much lower value which corresponds to the rate of amide hydrolysis, as the work with hydrochloric acid has shown. The ratio of k (nitrile) : k (amide) is evidently about 3 : 1, corresponding to an induction period of the observed magnitude. It is evident that for nitric acid concentrations commonly available, the above rate ratio varies from less than 1 : 100 (less than 4 N) to approximately 15 : 1 (estimated for 15 N).

The data for sulphuric acid indicate that at 10.60 N the ratio of the velocities of nitrile and amide hydrolysis is about 1 : 30. At 18.86 N the ratio is about 10 : 1 and determination of ammonia only leads to the evaluation

TABLE I

DATA ON THE NATURE OF CONSECUTIVE REACTIONS OF NITRILE AND AMIDE FOR THE DIFFERENT ACIDS

Acid	Acid concn., normality	A—Analysed for ammonia. AA—Analysed for ammonia + amide.	Temp., °C.	$k \times 10^3$ hr.$^{-1}$						
				% NH_3*						
				10-20	20-30	30-40	40-50	50-60	60-70	70-80
HBr	1.00**	A	86.5	0.996	0.964		0.942	0.931		
		AA	86.7	1.02	0.992	0.940	0.927	0.923	0.906	
	4.00	A	107.4	75.0	73.8		73.2	73.2		70.2
		AA	107.4	73.8	75.6	75.6	73.0	73.1	72.6	
	7.68	A	68.1	12.7	15.8	18.1		22.9	23.9	26.9
		AA	68.1	27.1	28.0	27.3	28.3	26.4		
HNO_3	1.00**	A	113.6	12.8 13.0	12.5		12.2	12.1		
	4.00	A	107.4		72.0 73.8		75.0	74.1 74.4	73.2	73.6
	13.01	A	80.5	12.0	18.2	20.6	22.5 23.0	23.7		
		AA	80.5	88.2	92.9	91.0	88.4	87.2	92.6	
H_2SO_4	2.00**	A	86.5	1.16	1.12 1.13	1.13	1.10			
	10.60	A	80.6	17.1	18.8	19.3	19.5	19.8	20.7	
		AA	80.6	20.5	20.7	20.6	20.2	21.2	20.9	21.1 19.8
	18.86	A	79.5	21.1	27.4 29.8		32.4	34.6		
		AA	68.1	93.6	93.7	95.4	95.6	93.5	95.5	93.2

* *Refers to runs analysed for ammonia only; given to indicate region where k was found.*

** *At these lower concentrations, depletion of the catalyst, by ammonia formation, causes a downward drift in the unimolecular velocity constants as the reaction progresses; the bimolecular values are quite satisfactory.*

of k for propionamide. Since the nitrile velocity continues to increase, while that of the amide decreases quite markedly (2) with increased acid concentrations, it appears that the hydrolysis in sulphuric acid covers the whole range k (propionitrile) $\ll k$ (propionamide) (2 N) to k (nitrile) $\gg k$ (amide) (estimated above 20 N). Karve and Gharpure (1) have investigated the hydrolysis of aliphatic nitriles in glacial-acetic–concentrated-sulphuric-acid medium over a range of sulphuric acid concentrations from 16.34 to 26.21 N. They found that only a small amount of amide was isolable in the reaction mixture. This behaviour differs from that observed here, probably because

their experimental conditions were different. The validity of the conclusions drawn here are supported by the fact that aliphatic nitriles, dissolved in 96% sulphuric acid, give rise almost quantitatively to the amide which can then be isolated (5, p. 139).

The unimolecular rate constants for each acid over a range of concentrations and temperatures are given in Table II. The average deviation from the mean in a given run was about 1 to 3%. No corrections have been applied

TABLE II

RATE CONSTANTS FOR PROPIONITRILE HYDROLYSIS AT VARIOUS ACID CONCENTRATIONS AND TEMPERATURES

Acid	Acid normality	Nitrile normality	Temp., ° C.	$k \times 10^2$ hr.$^{-1}$
Hydrobromic acid	1.00	0.4040	86.7	1.02
			100.4	3.80
			113.6	12.1
			124.8	31.2
	4.00	0.4063	78.7	4.58
			89.6	13.0
			100.7	37.5
			107.4	73.4
			109.6	84.9
	7.68	0.1638	48.7	3.65
			60.5	12.8
			68.1	27.4
			79.7	80.1
Nitric acid	1.00	0.4040	86.5	0.936
			100.4	3.81
			113.6	12.8
			124.8	33.1
	4.00	0.4067	78.7	4.66
			89.6	13.2
			100.4	38.8
			107.4	73.8
	13.01	0.2593	48.7	4.89
			60.5	15.1
			68.1	29.9
			80.5	90.0
Sulphuric acid	2.00	0.4057	86.5	1.15
			100.4	4.26
			113.6	14.2
			125.3	36.9
	10.60	0.5244	58.5	2.07
			69.9	7.09
			80.6	20.6
			92.4	66.0
	18.86	0.3883	48.7	12.3
			60.5	42.2
			64.6	66.8
			68.1	94.3

in this work for concentrations taken as at 25° C., or for the variation of collision number with temperature; for comparative purposes these errors should largely cancel. The Arrhenius lines were constructed from the data, and the values of E calculated. These, together with the corresponding values of A, are given in Table III, which also includes the previous results with hydrochloric acid for purposes of comparison. In calculating the A factor, the velocity constants have been expressed in seconds, and these values have been divided by the molarity of the acid to reduce the solutions to unit acid concentration, where sulphuric acid is considered to function as a monobasic acid. Although this procedure is a step in the right direction, it is of necessity arbitrary, particularly in the case of sulphuric acid, and may cause apparent deviation from a general shift in A (e.g., 1 and 4 N hydrobromic acid).

TABLE III

THE ARRHENIUS CONSTANTS FOR THE HYDROLYSIS OF PROPIONITRILE AT VARIOUS CONCENTRATIONS OF MINERAL ACIDS

Acid	Acid concentration, N	$\log_{10} A$	E, cal.
HBr	1.00	10.1	25,700
	4.00	10.2	25,300
	7.68	9.5	22,600
HNO_3	1.00	10.7	26,700
	4.00	10.7	26,100
	13.01	8.1	20,700
H_2SO_4	2.00	10.1	25,700
	10.60	10.1	24,400
	18.86	10.2	23,000
HCl	1.00	10.04	25,600
	4.00	9.95	24,800
	5.02	9.68	23,900
	6.48	8.92	21,800
	8.47	8.85	20,100
	10.13	8.78	18,900

It is seen from Table III that at the more dilute acid concentrations the activation energies are substantially the same. At higher concentrations, however, specific differences appear and considerable variation in activation energies at comparable concentrations is found.

The variation of rate with acid concentration at a given temperature is shown in Table IV, which also includes earlier data for hydrochloric acid. Velocities have been obtained from the Arrhenius lines. The relative rates for different acids at comparable concentrations will, of course, vary with temperature, particularly at high acid concentrations where the activation energies differ very appreciably.

It is evident that at lower concentrations the velocities are essentially the same. At higher concentrations, however, specific differences in rate become

TABLE IV

DATA FOR THE VARIATION OF RATE OF HYDROLYSIS WITH ACID CONCENTRATION FOR DIFFERENT ACIDS (87.2° C.)

Acid	$k \times 10^2$ hr.$^{-1}$					
	Acid molarity					
	1.00	4.00	5.02**–5.30†	6.48**–7.68*	8.48**–9.43†	13.01
HBr	1.14	11.4		157		
HNO_3	1.01	11.5				153
H_2SO_4	1.22		39.8		567	
HCl	1.14	12.1	28.5	120	1200	

** *HCl.* * *HBr.* † H_2SO_4.

evident, hydrochloric acid being the most efficient, followed by sulphuric, hydrobromic, and nitric acids in the order named. This behaviour has been noted previously (3), except for nitric acid.

The specific differences in rate increase with acid concentration may be accounted for by the specific variations of A and E. The reality of such changes in A and E for nitrile hydrolysis have been discussed previously (4). With sulphuric acid, the increase in rate with acid concentration follows the decrease in activation energy, but both the rate increase with acid concentration and the decrease in E are less marked than with hydrochloric acid. With hydrobromic acid, the value of A decreases at a concentration of 7.68 N, but the decrease in E is dominant and largely governs the rate. With nitric acid, a marked decrease in the value of A was observed at 13.01 N. The rate increase, therefore, is much slower than is indicated by the decrease in E.

It has thus been shown that in the acid catalyzed hydrolysis of propionitrile, the previously observed decrease in activation energy with increase of hydrochloric acid concentration is typical for mineral acids. As might be expected, the magnitude of the shift here is specific. Variation of an acid component of the critical complex would alter the characteristics of that intermediate. In addition, the general characteristics of the acid media at high acid concentrations are quite different and will result in specificity of the interaction between reactants, complex and medium.

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